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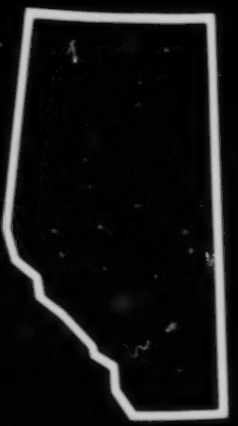

PROCEEDINGS

ACID FORMING EMISSIONS IN ALBERTA AND THEIR ECOLOGICAL EFFECTS

at the
WESTIN HOTEL
EDMONTON, ALBERTA
MARCH 9 - 12, 1982

Co-sponsored by Alberta Department of the Environment
Canadian Petroleum Association, Oil Sands Environmental Study Group

Symposium Workshop

Proceedings

ACID FORMING EMISSIONS IN ALBERTA AND THEIR ECOLOGICAL EFFECTS

at the

WESTIN HOTEL
Edmonton, Alberta

March 9 to 12, 1982

Co-sponsored by: Alberta Department of the Environment
Canadian Petroleum Association
Oil Sands Environmental Study Group

Organizing Committee: Dr. H.S. Sandhu (Co-chairman)
Dr. J.R. Clements (Co-chairman)
Ms. B.L. Magill

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PREFACE

The purpose of this Symposium/Workshop was to provide a means to exchange and synthesize environmental research information relating to acid-forming emissions in Alberta and their ecological effects. In particular, the information that has become available since the last Alberta Sulphur Gas Research Workshop III held in November of 1977.

Virtually all research results presented at the last Workshop focused upon sulphur dioxide and its effects. During the past two to three years, the focus has shifted to include acid deposition. This shift resulted from considerable technical and public interest in answering the question: "will the 'acid rain' problems of eastern North America and other parts of the world develop in western Canada." Although a large and definitive base of technical knowledge regarding acid deposition has not yet been developed in western Canada there was an apparent need to bring together environmental scientists and managers to discuss current information and to provide a basis for research directions for the future.

A joint industry-government organizing committee was formed by the Research Management Division of Alberta Department of the Environment, the Oil Sands Environmental Study Group, and the Research Advisory Council/ Canadian Petroleum Association, who sponsored and funded this Symposium/ Workshop.

After reviewing the format of the three previous Alberta Sulphur Gas Research Workshops, the organizing Committee decide this time to hold a combination of both symposium and workshop in order to accommodate the expanding scope of the research activities. In this way, the Symposium provided a formal forum for the presentation and discussion of research reports related to acid-forming emissions in Alberta and their ecological effects. The Workshops provided an opportunity for the intensive discussion of the issues arising from the Symposium, and for the formulation of research recommendations.

The intent of the Air, Aquatic, Terrestrial, and Health workshops was to:

1. Summarize the current knowledge;
2. Identify gaps in the current knowledge;
3. Provide direction for future research needs; and
4. Prepare a report on the above for the proceedings.

The organizing committee gratefully acknowledges the help of many people, who contributed to make the Symposium/Workshop a success. We especially would thank the Honourable J.W. Cookson, Minister of the Environment and Mr. L. Wilson, Vice President and General Manager of Operations, Syncrude Canada Ltd. for giving the opening remarks and welcoming the participants. We also extend our appreciation to Dr. J.M. Hales, Battelle-Northwest, Washington, and Dr. S.P. Gessel, University of Washington, for their keynote papers; and to Mr. J.P. Bruce, Assistant Deputy Minister, Environment Canada, for his luncheon address.

We wish to thank the chairpersons for overseeing the sessions and workshops. We also express our appreciation to the staff from both government and industry for their assistance throughout the Symposium/Workshop and in editing the preproceedings and proceedings. Their efforts contributed greatly to the overall success of the Symposium/Workshop.

Thanks are due to Ms. D.J. Lowry for her enormous help in editing these Proceedings.

June 1982

H.S. Sandhu
J.R. Clements
B.L. Magill

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KEYNOTE ADDRESS

PRECIPITATION SCAVENGING PATHWAYS AND MECHANISMS

A QUALITATIVE OVERVIEW

J. M. HALES[1]

Abstract

This paper provides a visualized overview of individual and composite mechanisms leading to the wet removal of pollution from the atmosphere. The subject is presented by disaggregating the composite scavenging process into several well-defined stages, which are examined individually to identify pertinent physical mechanisms. The paper concludes with a tabular summary of selected wet-removal models, which can be applied under appropriate circumstances for precipitation scavenging estimation and assessment.

---

[1] Atmospheric Sciences Department, Battelle-Northwest, Richland, Washington

1. INTRODUCTION

The objective of this paper is to provide a visual overview of the individual and composite processes leading to wet removal of pollution from the atmosphere. This is an appropriate and useful introductory topic for the present conference on acid-forming emissions for several reasons. Most importantly, it is crucial that both physical and life scientists working in this field possess a general awareness of these features, in order to exercise wise decisions in impact and data analysis, experiment design, and policy formulation. Secondly, many of the presentations of this conference deal with rigorous analyses of individual aspects of this subject, and it is useful to begin the proceedings with a somewhat less intensive but more all-encompassing overview. Finally, it is important to note that all predictive *models* of wet deposition are based upon human attempts to capture the essence of these mechanisms in a mathematical sense; therefore, to obtain any real understanding of the scope, limitations, and capabilities of present-day models one must necessarily begin by examining these key physical processes.

This discussion begins by disassembling the composite wet-removal process into four individual steps, which follow the fate of a pollutant particle as it approaches a storm, proceeds through a number of transitory stages, and ultimately wet-deposits at the Earth's surface. These four steps are then discussed on individual bases, in a manner which allows the reader to indentify key mechanisms responsible for accomplishing each of the transitions. The paper concludes by presenting a tabular summary of selected wet-deposition models, based upon various mathematical characterizations of these processes, which may be applied for wet-removal estimation under a variety of physical circumstances.

2. STEPS IN THE WET-REMOVAL SEQUENCE

In a very general sense there are four major events in which a pollutant particle or molecule* may participate, prior to its wet removal from the atmosphere; depicted pictorially in Figure 1, these are itemized as follows:

---

*This paper will treat precipitation scavenging in a somewhat general sense, with limited reference to specific types of pollutant material. The reader should continue to note, however, that the "pollutant

1-2. The pollutant and the condensed atmospheric water (cloud, rain, snow, ...) *must* intermix within the same airspace.
2-3. The pollutant *must* attach to the condensed-water elements.
3-4. The pollutant *may* react physically and/or chemically within the aqueous phase.
4-5. The pollutant-laden water elements *must* be delivered to the Earth's surface via the precipitation process.

The interaction diagram of Figure 2 gives a somewhat more detailed portrayal of these four major events. Here the individual steps are represented as transitions of the pollutant between various states in the atmosphere, and one can note that a multitude of *reverse* processes is also possible; thus it is not unexpected that a particular pollutant molecule may experience numerous cycles through this complex of pathways prior to deposition. Indeed, Figure 2 indicates that this cycling process may continue even after "ultimate" deposition. By pollutant off-gassing and other resuspension processes the deposited material can be re-emitted to the atmosphere, with the possibility of participating in yet another series of cycles throughout the scavenging sequence.

Another important feature of Figure 2 is its indication that, while physicochemical reaction within the aqueous-phase is potentially an *important* step in the scavenging process, it is not *essential*. This contrasts to the remaining forward steps which *must* take place, if scavenging is to occur. Despite this nonessential nature, this step is often of utmost importance in influencing scavenging rates, owing to its role in modifying reverse processes in the sequence. An example of this effect is the devolatilization of dissolved sulfur dioxide via wet oxidation to sulfate. This effectively eliminates gaseous desorption from the condensed water and enhances the overall scavenging rate as a result

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molecules" of primary concern in the present context are species associated with acid-base formation, such as SO_2, HNO_3, NH_3, sulfate nitrate, chloride, and so forth. A listing of ionic species important in this regard is presented in Table 1.

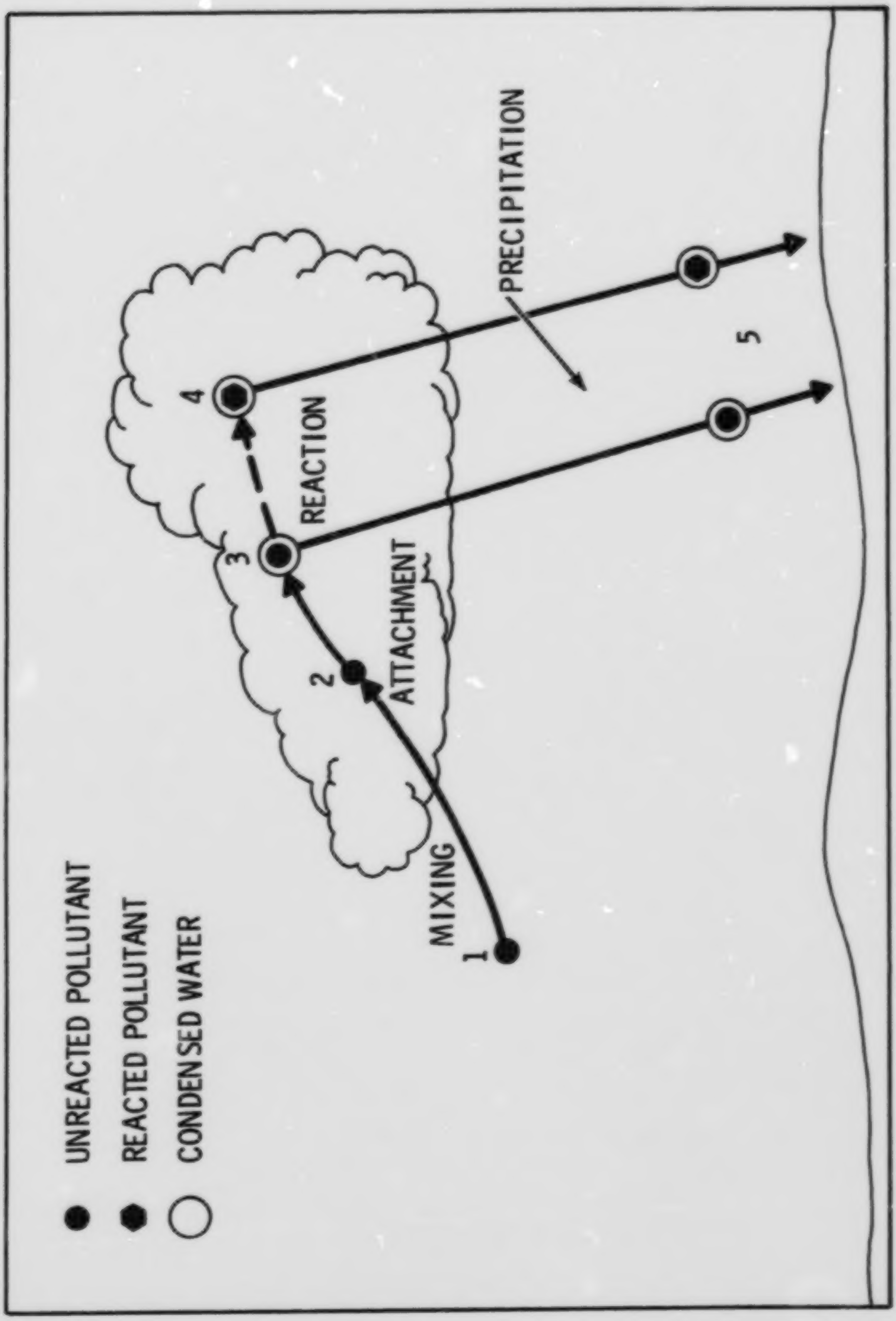
● UNREACTED POLLUTANT
⬢ REACTED POLLUTANT
○ CONDENSED WATER
1
MIXING
2
ATTACHMENT
3
REACTION
4
PRECIPITATION
5

FIGURE 1. Steps in the Scavenging Sequence: Pictorial Representation.

Table 1

SOME INORGANIC IONS
IMPORTANT IN PRECIPITATION CHEMISTRY

Cations	Anions
H^+	OH^-
NH_4^+	Cl^-
Na^+	NO_3^-
K^+	$SO_3^=$
Ca^{++}	$SO_4^=$
Mg^{++}	$PO_4^{\equiv}$
	$CO_3^=$

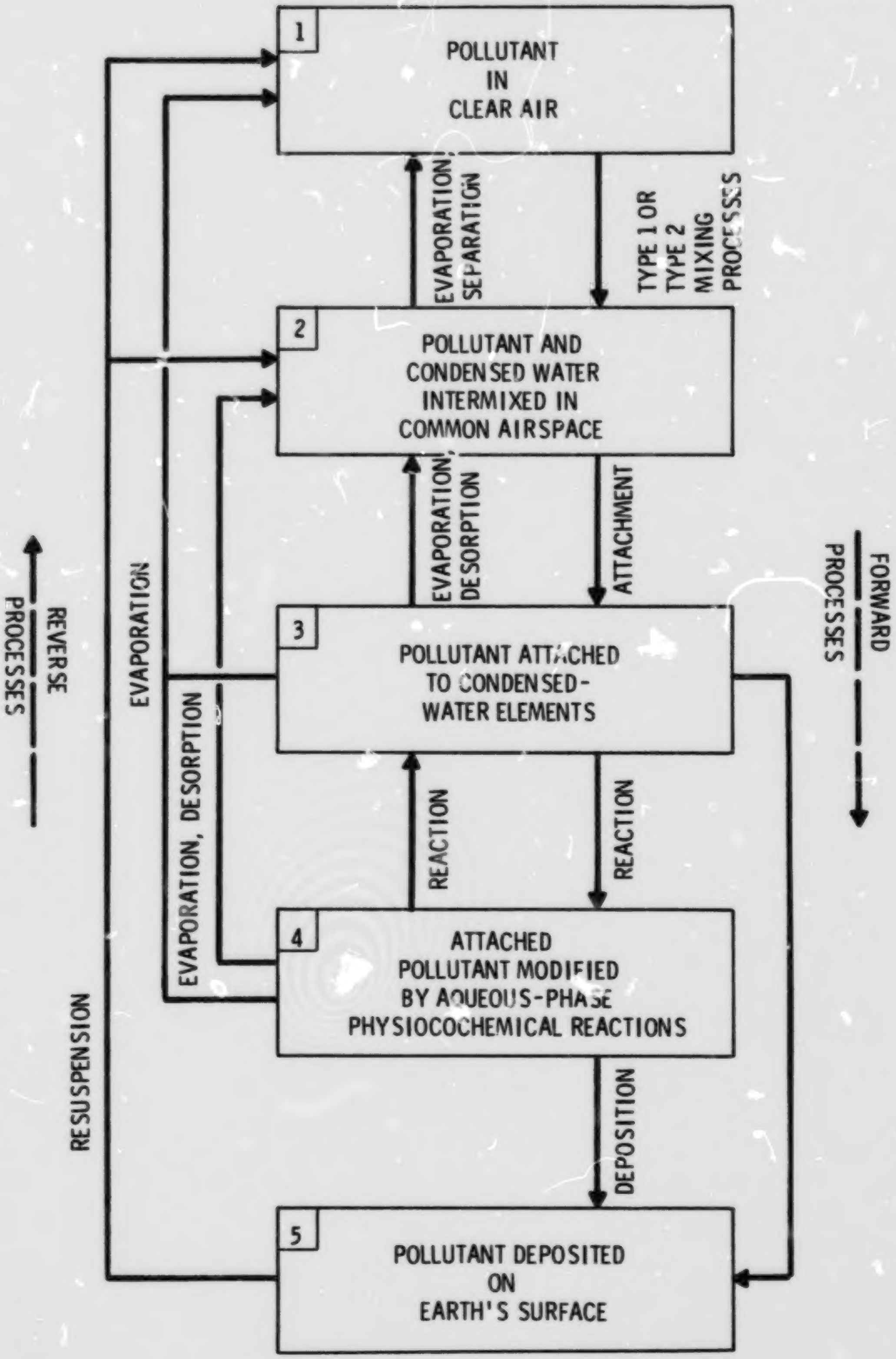
1
POLLUTANT IN CLEAR AIR
EVAPORATION, SEPARATION
TYPE 1 OR TYPE 2 MIXING PROCESSES
2
POLLUTANT AND CONDENSED WATER INTERMIXED IN COMMON AIRSPACE
EVAPORATION, DESORPTION
ATTACHMENT
3
POLLUTANT ATTACHED TO CONDENSED-WATER ELEMENTS
REACTION
REACTION
4
ATTACHED POLLUTANT MODIFIED BY AQUEOUS-PHASE PHYSIOCOCHEMICAL REACTIONS
DEPOSITION
5
POLLUTANT DEPOSITED ON EARTH'S SURFACE
EVAPORATION
EVAPORATION, DESORPTION
RESUSPENSION
REVERSE PROCESSES
FORWARD PROCESSES

FIGURE 2. Scavenging Sequence: Interaction Diagram.

From Figure 2 one can note also that precipitation scavenging of pollutant materials from the atmosphere is intimately linked with the precipitation scavenging of *water*. If one were to replace the word "pollutant" with "water vapor" in each of the steps, then (with the exception of box 4) Figure 2 would provide a general description of the natural precipitation process. In view of this intimate relationship, it is not surprising that pollutant wet-removal behavior tends to mimic that of precipitation; pollutant-scavenging efficiencies of storms, for example, are often observed to be similar to water-extraction efficiencies. This relationship is useful in the practical estimation of scavenging rates, and will reappear continually in the ensuing discussion of wet-removal behavior.

Figure 2 is interesting also because of its indication that, if some particular step in the diagram occurs particularly slowly compared to the others, then this step will dominate behavior of the overall process. This is similar to the "rate-controlling step" concept in chemical kinetics, and has been applied rather extensively in practical scavenging calculations [Slinn, (1974)]. Finally it is important to note that Figure 2 presents a framework for development and evaluation of mathematical models of scavenging behavior. Successful scavenging models *must* emulate these steps effectively, and tend to reflect the structure of Figure 2 as a result. Following sections of this presentation will address qualitative aspects of the scavenging sequence, in the order of their forward progress to ultimate deposition.

3. STEP 1-2: INTERMIXING OF POLLUTANT AND CONDENSED WATER

Upon first consideration one often is inclined to dismiss pollutant-condensed-water intermixing as an unimportant, or at least trivial step in the overall scavenging sequence. It is neither. In a statistical sense it usually is *not* cloudy or precipitating in the immediate locality of a freshly-released pollutant molecule; and typically this molecule must exist in the clear atmosphere for several hours or even days before it encounters condensed water with which it may co-mingle. This in itself establishes step 1-2 as a potentially important rate-influencing event. Moreover, this extended dry period typically presents the pollutant with significant opportunities to react and/or deposit via dry processes; thus the chemical makeup of precipitation is influenced profoundly by this preceding chain of events.

Significant insights to the behavior of step 1-2 can be gained via past analyses of storm formation [eg. Godske, et al. (1957)] and the atmospheric water cycle [Newell, et al. (1972)]. In addition, several statistical analyses of precipitation occurrence have emerged [Junge, (1974), Slinn, (1973), Rodhe and Grandell (1972, 1981), Baker, et al. (1979)] which have been applied as general interpretive descriptors of this step. These will not be examined in detail here; rather, we shall concentrate upon the mechanisms by which step 1-2 can occur, from a more pictorial viewpoint.

Two types of mixing processes exist in which pollutant and condensed water can come to occupy common airspace; these are

1. *Relative movement* of the initially unmixed pollutant and condensed water, in a manner such that they merge into a common general volume;

and

2. In situ *phase change* of water vapor, thus producing condensed water in the immediate vicinity of pollutant particles.

The relative importance of Type-1 and Type-2 mixing processes will depend to some extent on the pollutant. *If* a particular pollutant is easily scavengable and *if* precipitation is occurring at the pollutant's release location, then Type-1 processes are likely to contribute significantly. If these two conditionals are not met, however, then the pollutant will usually mix intimately with makeup water vapor for some future cloud, and Type-2 processes will predominate. As a global average it is not unreasonable to estimate that roughly 90% of all precipitation scavenging occurs as the consequence of a Type-2 process.

As indicated in Figure 2, reverse processes exist which can serve to reseparate pollutant and condensed water. Evaporation, for example, can reinject pollutant from cloudy to clear air, and relative motion such as precipitation "fall-through" can remove hydrometeors from contact with elevated plumes. Cloud formation - re-evaporation cycles are particularly significant in this respect. Junge, (1963), for example, estimates that a single water molecule will experience evaporation and condensation in about ten separate cloud systems before it is ultimately delivered to the Earth's surface as condensed water. The rate-influencing effect of such cycling in the context of precipitation scavenging is obvious.

Storm dynamics and storm climatology are crucially important factors in the context of step 1-2; and even though this subject is far too complex and vast to permit a really satisfactory treatment here, it deserves at least some mention at this point. For present discussion purposes it is useful to make the rather artificial distinction between two major types of storm systems: frontal and convective. Such a differentiation is problematic for a number of reasons. Convective storms, for example, are most often directly associated with some type of frontal disturbance, and well-identified frontal storms frequently contain significant convective flavor in their basic makeup. Moreover, a variety of additional storm types can exist, which may on occasion occur rather independently or else act as complicating factors superimposed on other systems. Orographic and lake-effect storms are particularly noteworthy in this regard. Regardless of these complicating factors, however, the above distinction is useful here for the purposes of illustrating the complexities and key features of the pollutant-ingestion (step 1-2) process.

Figure 3 presents a highly idealized representation of a frontal (or "cyclonic") storm system as it traverses the North American continent. Here the warm front and cold front are depicted by respective rounded and pointed symbols in the usual manner, and the total system can be envisioned as a "tongue" of warm air from the south intruding into a cold, northerly air mass. These frontal discontinuities

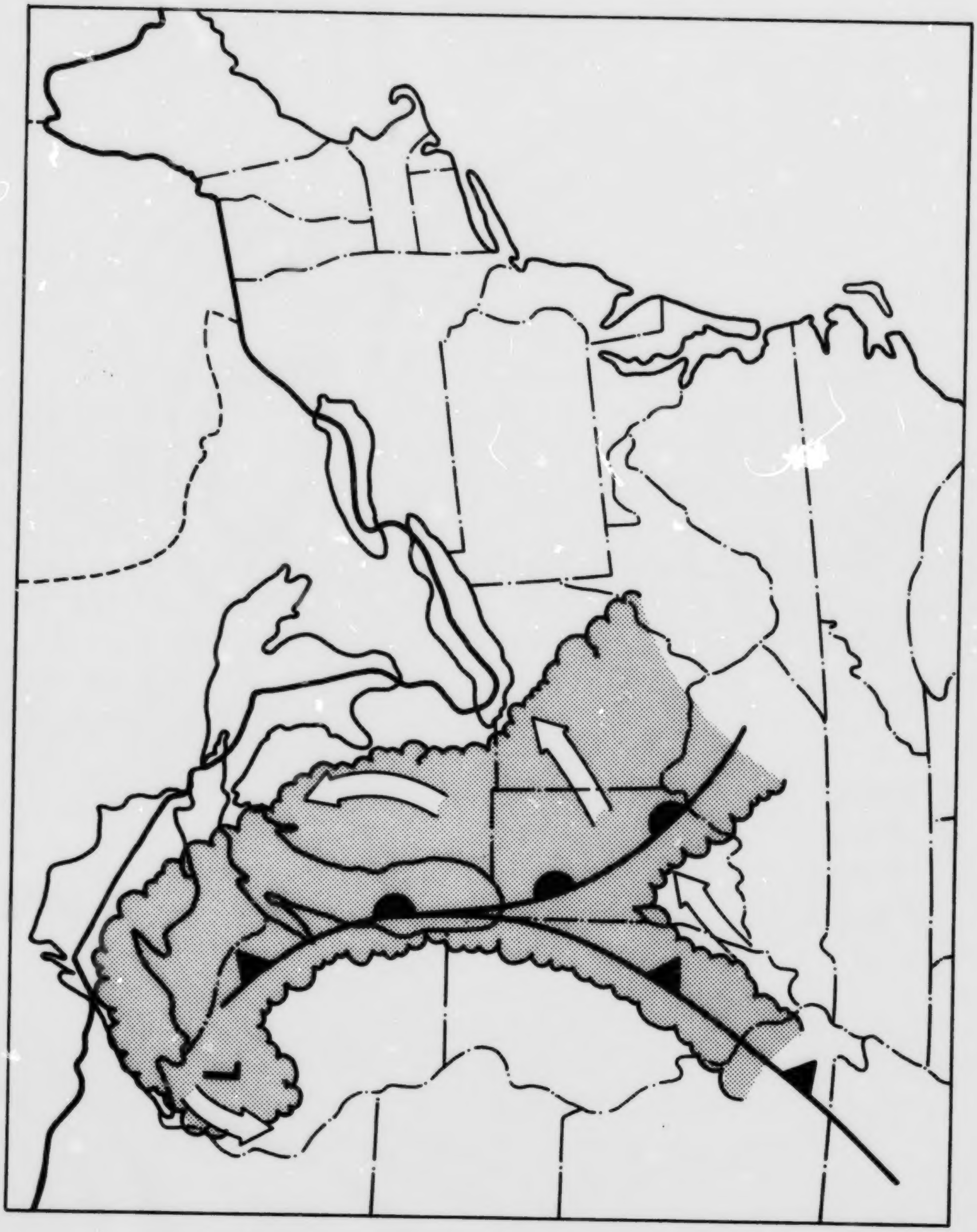

FIGURE 3. Schematic representation of an idealized frontal storm system.

are accompanied by clouds and precipitation systems, which are "fueled" by moist-air inflows from a variety of directions.

In the birth-death process of a frontal system it is usual for the cold front to overtake the warm front, ultimately leading to a weakening or a general collapse of the overall structure. The progression of this process is indicated in Figure 3 by the "occluded" region to the north, which terminates in the vicinity of a low-pressure area. This low-pressure zone, a typical feature of such systems, promotes a general counter-clockwise or "cyclonic" circulation of air throughout the frontal pattern, as indicated by the arrows.

It should be emphasized at this point that the general flow patterns shown in Figure 3 are gross indicators only, and radical shears and other spatial structure occur which serve to complicate these flows immensely. Some indication of this is given by the idealized vertical cross section of the warm front (see Section A-A' in Figure 3) shown in Figure 4. Here the moist "supply" air from the warm sector is shown to flow to the east, up and over the frontal surface, essentially as indicated in Figure 3. Flow in the cold wedge, however, is shown to change direction radically with height, adding considerable complexity to the general structure. It should be noted as well that Figure 4 is a highly simplified representation of actual behavior in warm-front systems. Considerable additional complexity, including rain bands, isolated showers, and complex flow dynamics usually appear to significantly complicate the structure of actual systems.

Some indication of climatological behavior of North-American frontal-storm systems can be obtained from Figure 5, which represents major "cyclone tracks" across the continent. The arrows represent climatologically-prefered pathways of low-pressure centers associated with cyclonic systems (cf. Figure 3) and as such are *not* intended to depict wind patterns. By applying these tracks in conjunction with idealized cyclonic-storm flow patterns, however, can generate at least a qualitative impression of input flows and generalized behavior of such systems.

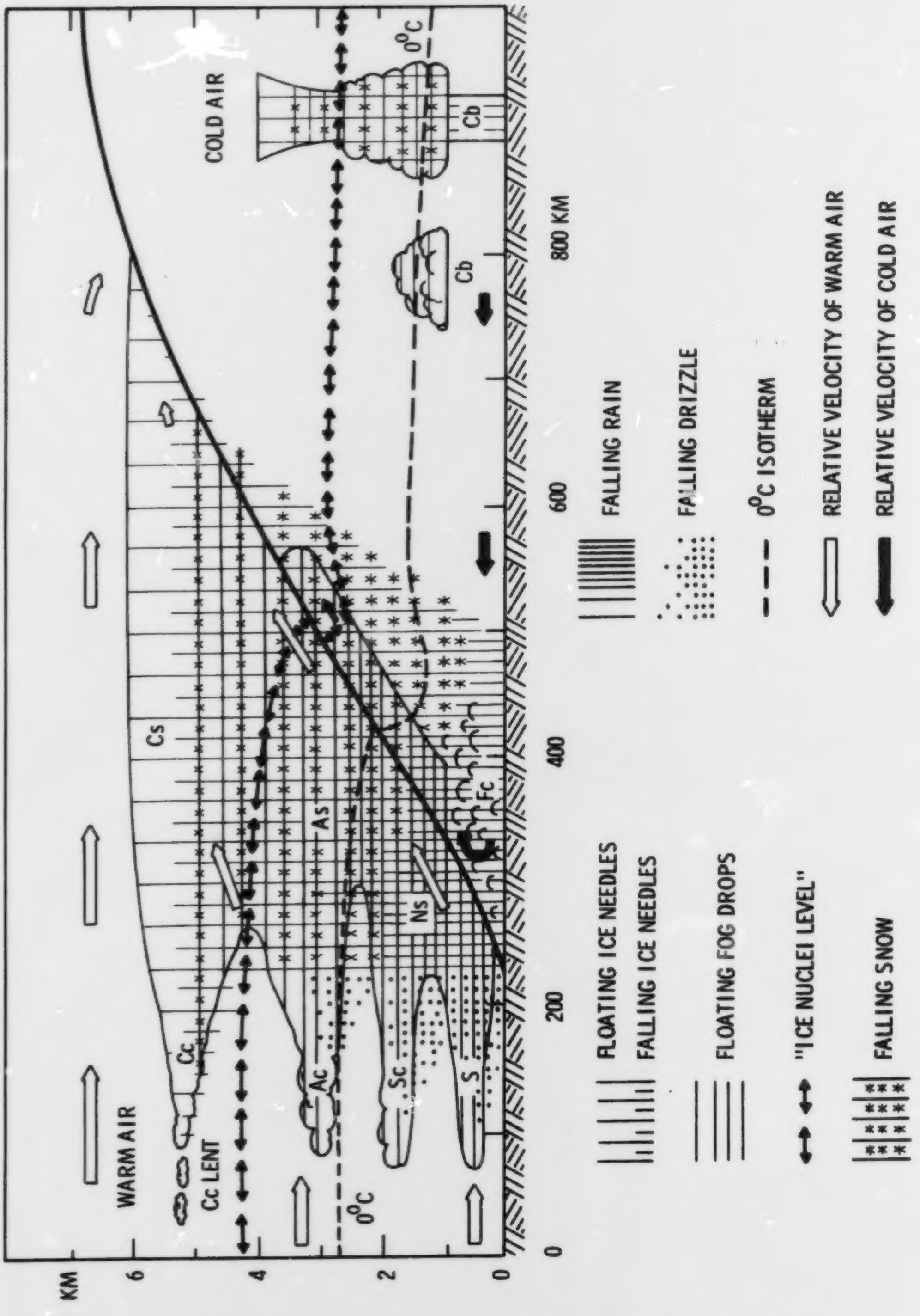
KM
6
4
2
0
0
200
400
600
800 KM
WARM AIR
COLD AIR
Cc LENT
Cc
Ac
Sc
S
Cs
As
Ns
Fc
Cb
Cb
0°C
0°C
0°C
FLOATING ICE NEEDLES
FALLING ICE NEEDLES
FLOATING FOG DROPS
"ICE NUCLEI LEVEL"
FALLING SNOW
FALLING RAIN
FALLING DRIZZLE
0°C ISOTHERM
RELATIVE VELOCITY OF WARM AIR
RELATIVE VELOCITY OF COLD AIR

FIGURE 4. Idealized cross-sectional schematic of a warm front. (adapted from Godoke et al. 1957)

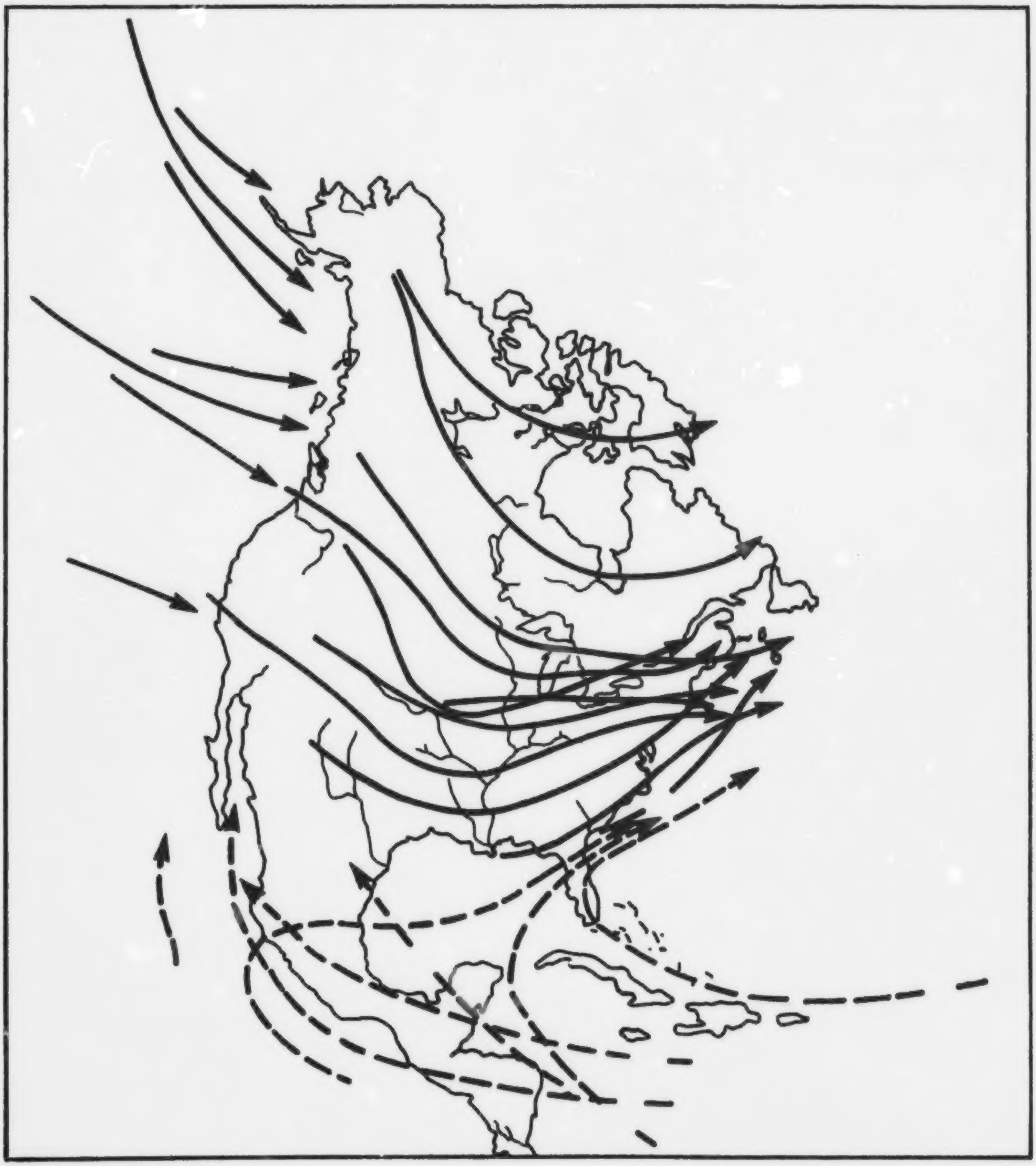

FIGURE 5. Major climatological storm tracks for the North American continent Adapted from Haurwitz and Austin (1944).

Several key points regarding step 1-2 processes and wet-removal in general can be made from the above discussion. The first of these is that flow patterns associated with frontal-storm systems tend to be exceedingly complex. From this one can appreciate the high degree of uncertainty associated with typical constant-level trajectory models, which depend upon loosely-interpolated wind data, when applied for wet-removal calculations. The above figures also provide ample illustration of the previous assertion that Type-2 mixing processes should provide the predominant mode of pollutant ingestion. From Figure 4, for example, it seems evident that most of the pollutant should enter the storm as an intimate mixture with supply water vapor, and become associated with a liquid-water system as condensation occurs.

An idealized schematic of a typical *convective* storm system is shown in Figure 6. From this schematic it can be noted that, while flow patterns are more localized and in general quite different from stable frontal storms, these systems share the characteristics of complex dynamic behavior, and the co-processing of pollutant/water-vapor laden air. Again the Type-2 mixing process emerges as a dominant mechanism for completing step 1-2 of the scavenging sequence.

As a conclusion to this discussion of the pollutant - liquid-water comixing process one can conclude that step 1-2 is an essential element in the scavenging sequence, that it can be rate-limiting under some circumstances, and that it is generally immensely complicated. Much remains to be learned in this important area before really reliable regional scavenging models can be developed.

4. STEP 2-3: ATTACHMENT OF POLLUTANT TO CONDENSED WATER ELEMENTS

The microphysics of the pollutant-attachment process have been the subject of extensive research, and numerous reviews of this area have been prepared [eg. Slinn, (1981), Slinn and Hales, (1982), Hales, (1981), Pruppacher and Klett (1978), Dingle et al. (1973), Junge, (1963), Davies (1966)]. In the context of Figure 1, this process is complicated somewhat in the sense that, depending upon the particular attachment mechanism, step 2-3 may occur either *simultaneously* or *consecutively* with step 1-2.

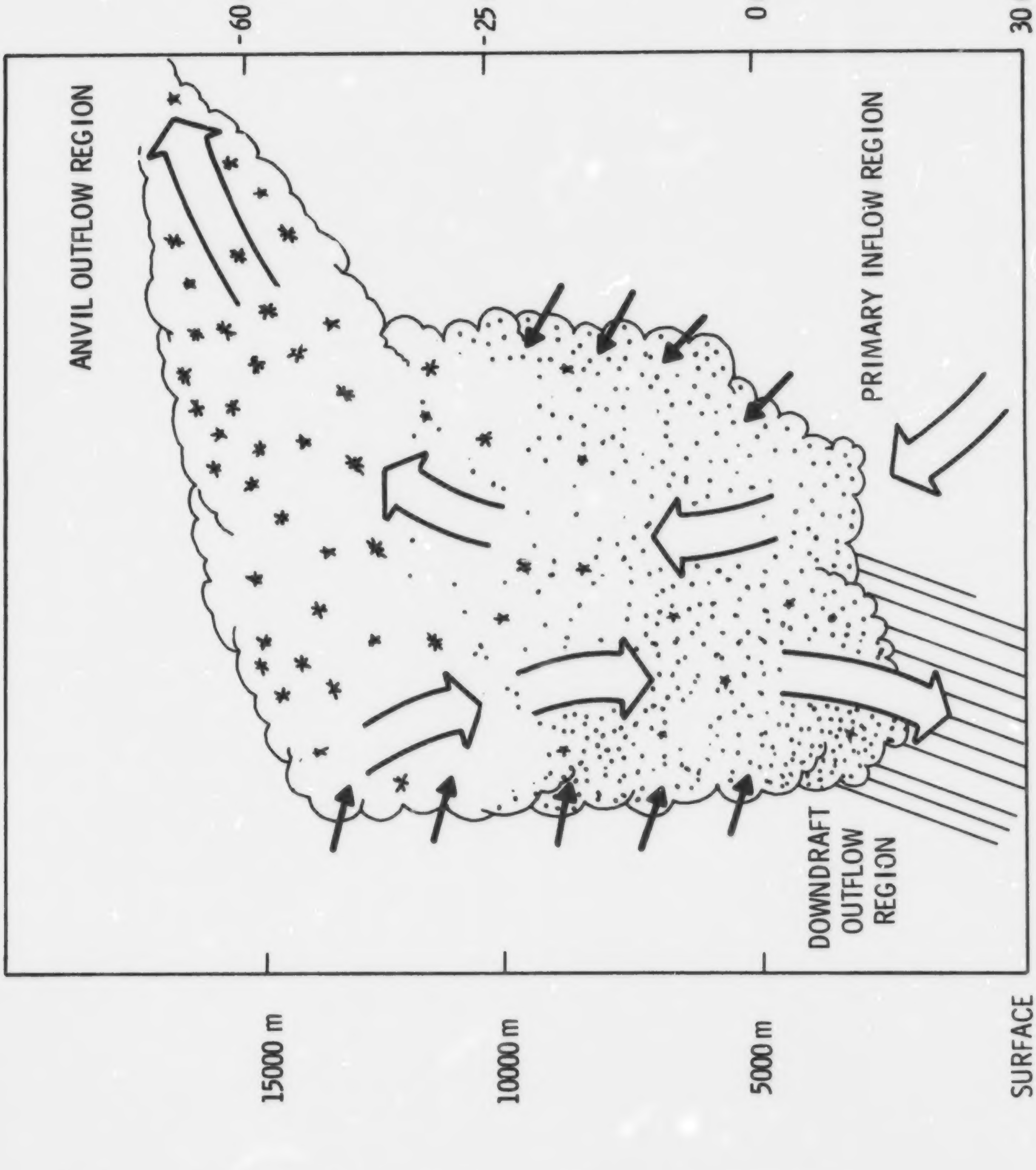
ANVIL OUTFLOW REGION
PRIMARY INFLOW REGION
DOWNDRAFT OUTFLOW REGION
-60 C
-25 C
0 C
30 C
15000 m
10000 m
5000 m
SURFACE

FIGURE 6. Idealized representation of a typical convective storm.

Simultaneous comixing and attachment occur in the case of cloud-particle *nucleation*. This is a phase-transformation (Type-2) process wherein water molecules, thermodynamically inclined to condense from the vapor phase, migrate to some suitable surface for this purpose. Pollutant aerosol particles provide such surfaces within the air parcel, and the consequence is a cloud of droplets (or ice crystals)* containing attached pollutant material.

It is important to recognize that different types of aerosol particles possess different capabilities to nucleate cloud elements and grow by the condensation process. As a consequence there is typically a competition for water molecules among the aerosol and associated cloud particles; some will capture water with high efficiency and grow substantially in size. Others will acquire only small amounts of water, and still others will remain essentially as "dry" elements. In addition, some particles may nucleate ice crystals, while others will be active only for the formation of liquid water. The nucleating capability of a particular aerosol particle is determined by its size, its morphological characteristics, and its chemical composition. Various aspects of this subject are discussed at length in standard cloud-physics textbooks [eg. Pruppacher and Klett, (1978), Mason, (1971)] and in the periodical literature [eg. Fitzgerald, (1974)].

An additional important aspect of the cloud-droplet nucleation and growth process is the fact that once initiated, cloud-droplet growth does *not* proceed instantaneously to some sort of thermodynamic equilibrium. Because of diffusional constraints on delivering water molecules from the surrounding atmosphere, droplet growth slows appreciably as droplet sizes increase [cf. Slinn, (1981)]. Superimposition of this lag on the continually fluctuating environment of a typical cloud results in a dynamic and complex physical system.

---

*At this point it is important to note that aerosols can participate in several types of phase transitions in cloud systems. These include vapor-liquid, vapor-solid, and liquid-solid transitions, in addition to a subset of interactions between numerous solid phases. Particles active as ice-formation nuclei are generally much less abundant than those active as droplet (or "cloud-condensation") nuclei. As will be demonstrated later, the relative abundance of ice nuclei can have a profound effect upon precipitation-formation processes and related scavenging phenomena.

Finally, it should be noted that the competitive nature of the cloud-nucleation process results in significant impacts by the pollutant on the basic character of the cloud itself. If the local aerosol were populated solely by a relatively small number of large, hygroscopic particles, for example, one would expect any corresponding cloud to be composed chiefly of low populations of large droplets. If on the other hand the local aerosol were composed of large numbers of small, nonhygroscopic particles, then any corresponding cloud should contain larger numbers of smaller droplets.

This is precisely what is observed in practice. Unpolluted marine atmospheres, for example, contain large sea-salt particles as a primary component of their aerosol burden. Warm marine clouds are noted for their large drop sizes and their corresponding capability to form precipitation easily. Continental clouds, on the other hand, are typically composed of larger populations of smaller droplets. Figure 7, which was prepared on the bases of results published by Squires (1959), provides a good example of this point. Here measured convective-cloud droplet spectra are compared for two different cloud systems. The continental air-mass cloud exhibits a distinct tendency toward smaller drop sizes and larger populations, as compared to its maritime counterpart. It is interesting also in this context to note the estimates of Junge (1963) with regard to relative amounts of aerosol participating in the nucleation process. Junge suggests that while 50 to 80 percent of the mass of continental aerosols can be expected to participate as cloud nuclei, as much as 90 to 100 percent of maritime aerosols can become actively involved.

As a concluding note in the context of nucleating capability and water competition it should be pointed out that acid-forming particles, by their very nature, are chemically competitive for water vapor and thus tend to participate actively as cloud-condensation

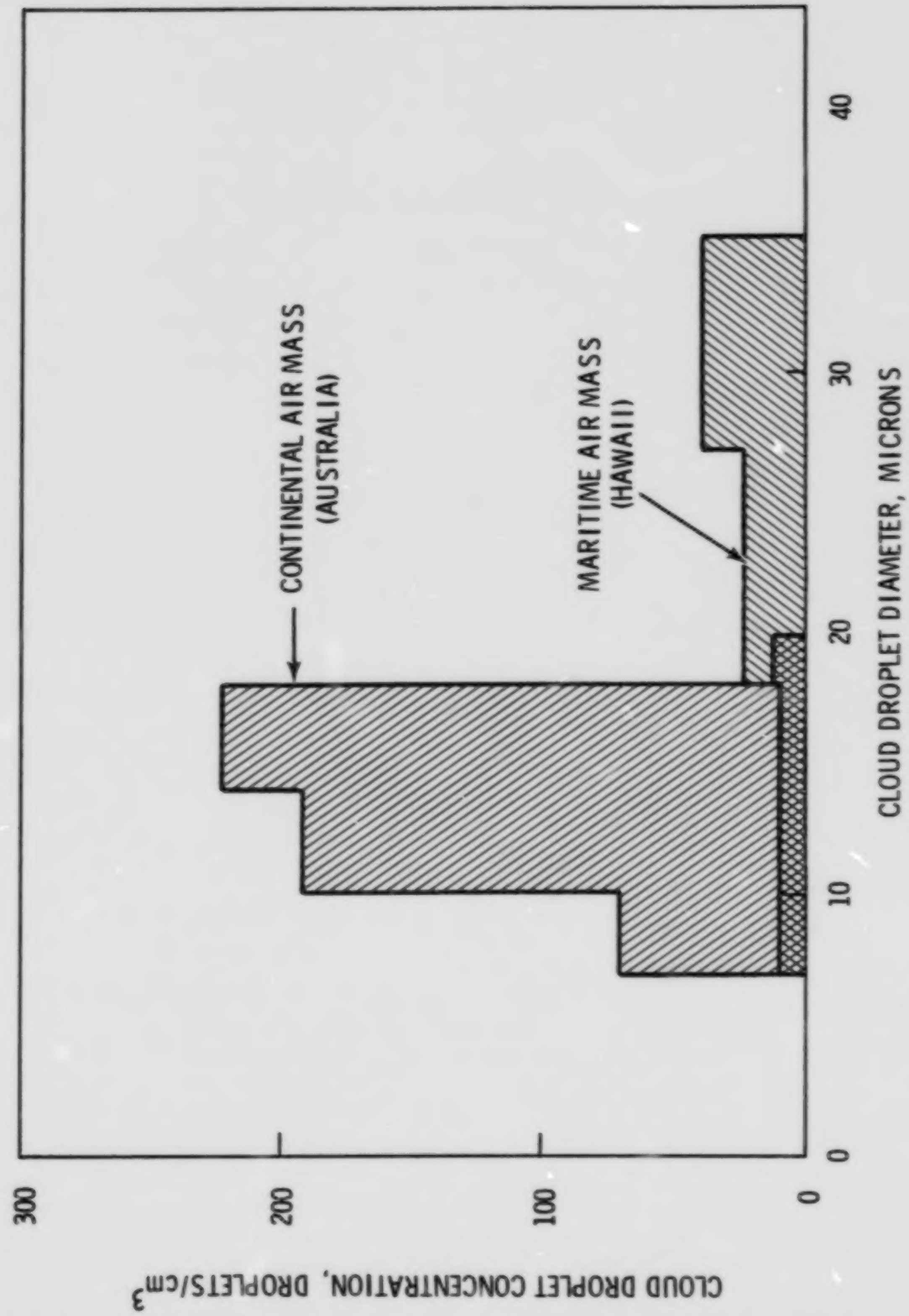

FIGURE 7. Cloud droplet spectra in convective cloud forms in maritime and continental air masses. (adapted from Squires 1959)

nuclei. This attribute tends to enhance their propensity to become scavenged early in storm systems and has a significant effect on the nature of the acid-rain formation process.

There are numerous mechanisms by which pollutants can attach to cloud and precipitation elements *after* the elements already exist, and thus in a manner which is *consecutive* with Step 1-2. These mechanisms are itemized in the following paragraphs.

Diffusional attachment, as its name implies, results from diffusional migration of the pollutant through the air to the water surface. This process may be effective both in the case of suspended cloud elements and falling hydrometeors. It depends chiefly upon the magnitude of the pollutant's molecular (or Brownian) diffusivity; and since diffusivity is inversely related to particle size, this mechanism becomes less important as pollutant elements become large. For all practical purposes diffusional attachment can be ignored for particle sizes above a few tenths of a micron.

In concordance with Fick's law [Bird, et al. (1960), diffusional transport to a water surface is dependent as well upon the pollutant's concentration gradient in the vicinity of this surface. Thus if the cloud or precipitation element can accommodate the influx of pollutant readily, it will effectively depopulate the adjacent air, thus making a steep concentration gradient and encouraging further diffusion. If for some reason (eg. particle "bounce off" or low gas solubility) the element cannot accommodate the pollutant supply, then further diffusion will be discouraged. If the cloud or precipitation element, through some sort of outgassing mechanism, *supplies* pollutant to the local air, then the concentration gradient will be reversed and diffusion will carry the pollutant *away* from the element.

Mixing processes inside of cloud or precipitation elements play an important role in determining the accommodation of gaseous species. If mixing is slow, for example, it is likely that the element's outer layer will saturate with pollutant and thus inhibit further attachment processes. This is quite often a limiting factor in cases involving gas scavenging by ice crystals. Internal mixing occurs as a consequence of diffusion and fluid circulation, and has been analyzed at length by Pruppacher and his coworkers [cf. Pruppacher and Klett, (1978)].

In general it may be stated that diffusional attachment processes are sufficiently well understood to allow their mathematical description with reasonable accuracy, and numerous references are available as guides for this purpose [eg. Pruppacher and Klett, (1978), Slinn, (1981), Hales, (1981)].

Inertial attachment processes depend upon motions of pollution particles and scavenging elements relative to the surrounding air, which arise by virtue of the fact that both have finite volume and mass. The most important example of inertial attachment is the *impaction* of aerosols on falling hydrometeors. Here the hydrometeor (because of its mass and volume) falls by gravity, sweeping out a volume of space. Some of the aerosol particles (because of their mass) cannot move with the flow field sufficiently rapidly to avoid the hydrometeor, and thus are impacted. It should be noted here that in principle impaction could occur, even if the aerosol particles were point masses with zero volume. Assigning a volume to a particle further increases its chance of collision, simply on the basis of geometric effects. The inclusion of aerosol volume in this context has been generally referred to as *interception* in the past literature.

The effectiveness of impaction and interception depends upon both aerosol-particle and hydrometeor size; and mathematical formulae exist which can be utilized conveniently to estimate the magnitudes of these processes [eg. Slinn, (1981), Hales, (1981)]. These effects generally become unimportant for aerosols less than a few microns in size. In this context it is interesting to note that a two-stage capture mechanism can exist, in which a small aerosol first grows via nucleation to form a larger droplet, which can be captured by inertial attachment in a secondary process. This two-stage process has been postulated as an important mechanism in below-cloud scavenging [Radke, et al. (1978), Slinn, (1981)]. It is also an essential factor in the in-cloud generation of precipitation, and is generally referred to as *accretion* under these circumstances.

A second example of inertial attachment is the *turbulent* collision. In this case the particles and scavenging elements, subjected to a turbulent field, collide because of dissimilar dynamic responses to velocity fluctuations in the local air. This scavenging mechanism is thought to be of secondary importance and has received comparatively little attention in the past literature, although some recent theoretical analyses have suggested it to be significant for specific drop size-particle size ranges.

Upon considering diffusional and inertial attachment processes in retrospect one can note that, while these mechanisms are efficient for capturing very fine and very coarse particles, respectively, a region of low efficiency should exist in the 0.1-5 micron range where neither mechanism is effective. This effect is shown schematically in Figure 8. Because its importance to scavenging was first recognized by Greenfield (1957), it has become known generally as the "Greenfield gap." Depending upon circumstances there are several additional attachment mechanisms (including the two-stage nucleation-impaction mechanisms mentioned earlier) which can serve to "fill" the Greenfield gap. Some of the more important of these are itemized in the following paragraphs.

Diffusiophoretic attachment to a scavenging element can occur whenever the element grows via the condensation of water vapor. In effect the flux of condensing water vapor "sweeps" the surrounding aerosol particles to the element's surface. In the context of a competitive cloud-element system where some droplets grow while others evaporate, diffusiophoresis can be a rather important secondary attachment mechanism. This is particularly true when the cloud contains mixtures of ice and liquid. Under such conditions the ice crystals have a pronounced tendency, owing to their lower equilibrium vapor pressure, to gain water at the expense of the droplets. Known as the *Bergeron-Findeisen* effect, this process is important in precipitation formation as well as in diffusiophoretic enhancement.

Thermophoretic attachment results from a temperature gradient which is downward in the direction of the capturing element. Here the element acts essentially as a miniature thermal precipitator; warmer gas molecules on the outward side of the aerosol particle impart a proportionately large amount of momentum, resulting in a driving force toward the capturing element.

Thermophoresis depends directly upon the temperature gradient in the vicinity of the capturing element. In cloud and precipitation systems local temperature gradients are caused most often by evaporation/condensation effects; thus thermophoresis is usually strongly associated with diffusiophoresis,* and in fact these two processes often tend to counteract each other.

At the present time the theory of diffusiophoretic/thermophoretic attachment is at a state where reasonably quantitative assessments can be made for simple systems such as isolated droplets [Pruppacher and Klett, (1978), Davies, (1966), Slinn and Hales, (1971)]. Rough estimates are possible also for more complex and interactive cloud/precipitation systems, but much remains to be done to bring our knowledge to a really satisfactory state in this area.

Electrical attachment of aerosol particles to cloud and precipitation elements has been the subject of continuing study over the past three decades, and our understanding of this process is currently at a state where relationships between aerosols and isolated drops can be quantified with reasonable accuracy [cf. Wang and Pruppacher, (1977)]. In general electrical charging of cloud and/or precipitation elements must be moderately high for electrical effects to become competitive with other capture phenomena; although such charging is certainly possible in the atmosphere--particularly in convective-storm situations. Our understanding of electrical deposition in clouds of interacting drops is still at a relatively unsatisfactory stage of development.

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*As noted by Slinn and Hales (1971), inappropriate treatment of this relationship has caused erroneous conclusions to be drawn in some of the past literature. The reader should be cognizant of this if more detailed pursuit is intended.

As a conclusion to this discussion of attachment processes it is appropriate to note that, while the mechanisms have been presented here on a more-or-less individual basis, they tend in actuality to proceed in a simultaneous and competitive manner. In the context of atmospheric cleansing this is a fortunate circumstance, because some mechanisms tend to "cover" in physical situations where others are ineffective. Figure 8 gives an excellent illustration of this point. Here theoretical attachment efficiencies appropriate to a 0.31 mm radius raindrop are presented for various electrical and relative-humidity conditions, demonstrating the capability of phoretic and electrical mechanisms to "bridge" the Greenfield gap. This simultaneous and competitive interaction of mechanisms serves to complicate profoundly the mathematics of the scavenging process, and lends an additional degree of difficulty to the problem of scavenging calculations.

5. STEP 3-4: AQUEOUS-PHASE REACTIONS

Aqueous-phase reaction chemistry in the context of precipitation scavenging has undergone a rather tortuous pattern of review, rereview, revision, and recycling of this process, with the result that we still know distressingly little regarding in-cloud reaction phenomena. In view of these features this paper will refrain from yet another attempt at review and instead refer the reader to the recent excellent compilation by Graedel and Weschler (1981). In this context, however, it is important to reemphasize the point that although (in the sense of Figure 2) aqueous-phase reactions are not *essential* to the scavenging process, they can be *highly important* in determining its rate. As noted previously, these reactions often can have the effect of stabilizing the captured material within the condensed phase, and thus enhancing the scavenging efficiency appreciably. There is much to be learned before this important aspect is brought to a satisfactory stage of understanding.

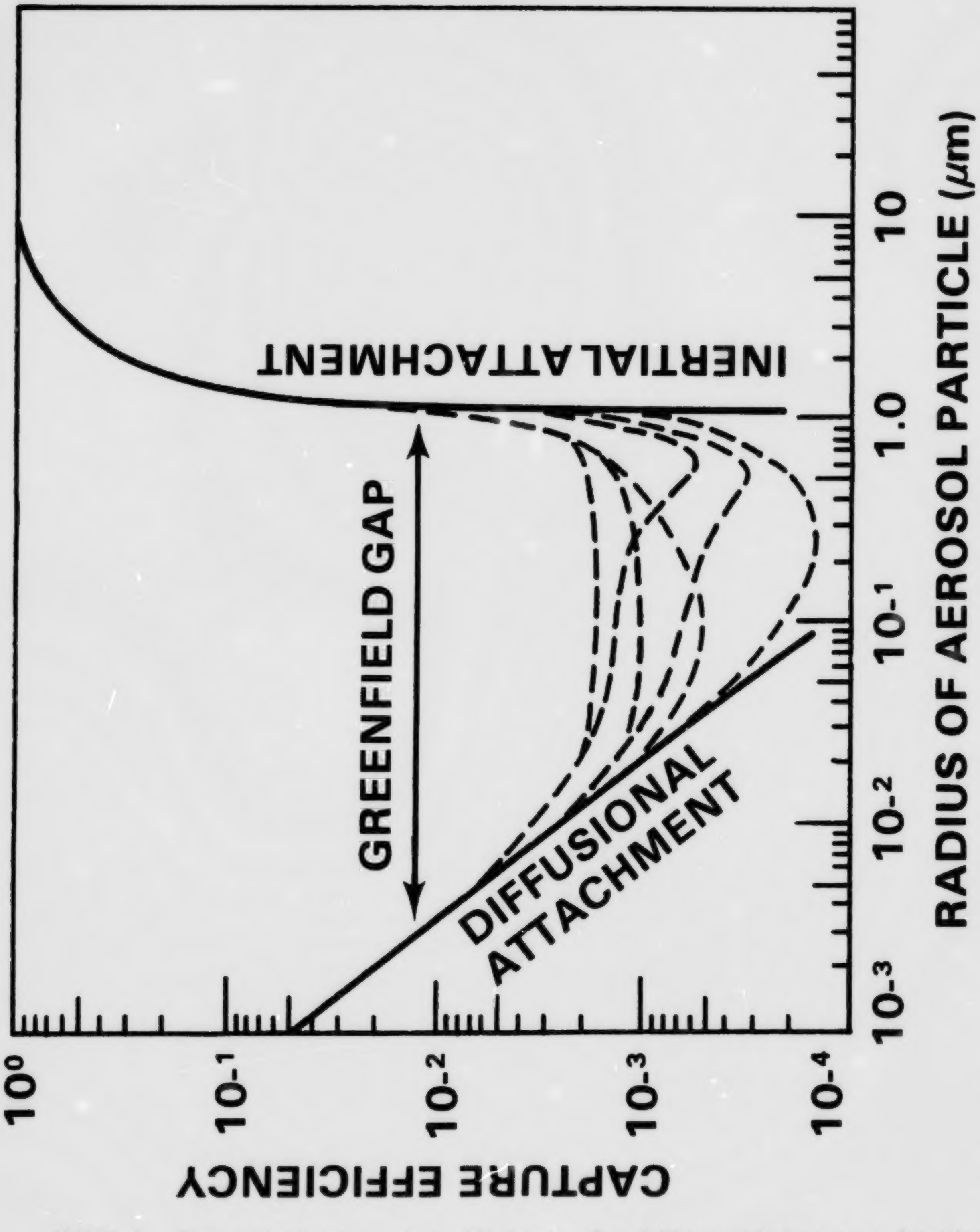

FIGURE 8. Theoretical scavenging efficiency of a falling raindrop as a function of aerosol particle size. Adapted from curves given by Pruppacher and Klett (1978). Dashed lines correspond to contributions by electrical and phoretic effects under chosen conditions.

6. STEP 4-5: DEPOSITION OF POLLUTANT WITH PRECIPITATION

Although a variety of alternative mechanisms exists (eg. impaction of fog on vegetation), the predominant means for depositing pollutant-laden condensed water to the Earth's surface is sedimentation. Sedimentation rates depend upon hydrometeor fall velocities, which depend in turn on hydrometeor size; thus the processes by which the pollutant-laden cloud droplets grow to precipitation elements emerge as major determining factors in the context of this final stage of the scavenging sequence.

With reference to the interaction diagram in Figure 2 it is seen that, once attached to condensed water, a pollutant molecule has several alternative pathways for action. If the captured pollutant possesses some degree of volatility it may desorb back into the gas phase. Reverse chemical reactions may occur. Evaporation of the condensed water may, in effect, "free" the pollutant to the surrounding gaseous atmosphere. This multitude of pathways results in an active *competition* for pollutant; and it is readily apparent that if the precipitation stage of the scavenging sequence is to be effective, it must interact successfully within this competitive framework.

It is worthwhile to note once again in this context that, besides competing actively for pollutant, the above forum of interactions produces a vigorous competition for *water*. This parallel relationship between pollutant scavenging and water scavenging, apparent in some of the preceding discussion regarding attachment processes, can be drawn even more emphatically when considering precipitation processes. The following paragraphs provide a brief overview of some of the more important mechanisms in this regard.

Once initial nucleation has occurred, cloud particles may grow further by *condensation* of additional water vapor. Net condensation will occur to the surface of a cloud element whenever water vapor molecules can find a more favorable thermodynamic state in association with it; and because clouds contain varieties of makeup elements having different thermodynamic characteristics, a competition for water vapor usually exists. Such interactions are discussed at length in standard textbooks [Mason, (1971), Pruppacher and Klett, (1978)], and Slinn, (1981) has developed a conceptual scavenging model in which condensational growth is an important rate-limiting step.

Thermodynamic affinity for water-vapor molecules depends upon the cloud-element's size, its pollutant burden, and its physical structure. These latter two factors often influence precipitation characteristics profoundly. In particular, the favored thermodynamic state of a water molecule in association with an ice crystal (as compared with a supercooled water droplet) results in rapid competitive growth of ice particles in mixed-phase clouds. This Bergeron-Findeisen process has been mentioned already in the context of diffusiophoretic and thermophoretic transport. Growth of large cloud elements via this process is the primary reason that ice-containing clouds tend to be so strongly effective as generators of precipitation water.

A further mechanism by which suspended cloud droplets can grow to form precipitation elements is *coagulation*. This process occurs via the collision of two or more cloud elements to form a new element containing the total mass (and pollutant burden)* of its predecessors. Coagulation occurs over size-distributed systems of cloud elements by a variety of physical mechanisms, and because of this it is a rather poorly-understood and mathematically complex process. Comprehensive analyses of coagulation processes have been performed by Berry and Reinhardt (1974). Coagulation can be considered to be an important initiator of precipitation in single-phase clouds (water or ice). In mixed-phase clouds the Bergerson-Findeison process can be expected to dominate.

Once a moderate number of precipitation-sized elements have been generated, the process of *accretion* rapidly begins to dominate as a means for generating precipitation water. As noted previously in the context of the "two-step" attachment mechanism, this process occurs by the "sweeping" action of large hydrometeors falling through the field of smaller elements, attaching them on the way. As was the case with coagulation, the accretion process tends to accumulate the pollutant burden of all collected elements.

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*It is interesting to notice in this context that while coagulation tends to accumulate nucleated pollutants, the Bergeron-Findeisen process tends to re-liberate nucleated pollutants to the air.

Accretion can occur via drop-drop, drop-crystal, and crystal-crystal interactions. Drop-crystal interactions are particularly important in mixed-phase clouds; when supercooled droplets are accreted by falling ice crystals, the process is usually referred to as *riming*.

As was the case with virtually all the preceding steps in the scavenging sequence, there are numerous conditions where step 4-5 can act as a rate-limiting feature for the composite wet-removal process. An extreme case, for example, is a cloud system which is producing virga, but not allowing precipitation to reach the ground. Quite obviously all of the preceding steps could be occurring with high efficiency, and yet wet removal would not occur. From this example it is not difficult to imagine less extreme situations where precipitation reaches the ground, but the scavenging sequence is still largely limited by this final step. Depending upon the nature of the mathematical characterization, this step can emerge as a key feature of wet-removal models.

7. CONCLUSIONS: COMPOSITE INTERACTIONS AND WET-REMOVAL MODELS

This qualitative review of wet-removal pathways has been presented using a simple classification scheme to elucidate individual mechanisms, and to indicate their relative importance within the overall precipitation-scavenging process. Despite this individualized approach, however, it is important to emphasize that wet removal is typically a highly interactive, composite process (cf. Figure 2), and that quantitative mathematical models of this phenomenon must reflect this feature in their basic makeup.

As indicated by the selected listing in Table 2, a profusion of wet-removal models is available for use in applied scavenging calculations, and guidelines exist elsewhere (Hales (1981)) to aid in their selection in individual cases. These models differ from one another in many significant respects. Most important, however, are those differences in simulation of the microphysical and dynamical processes discussed in the above sections, and their combination to provide composite characterizations. Both of these areas contain rather high levels of uncertainty, and result, typically, in considerable deviations between the results of various models. Much remains to be accomplished in this important research area before wet-removal modeling can be considered to be in a truly satisfactory state.

Table 2. Pertinent Literature References for Wet-Removal Models

Model	Type of Balance Equation(s)	Mechanism(s)	Typical Application	Pertinent References
1. Classical Washout Coefficient	Material (Differential)	Irreversible Attachment	Below-cloud scavenging of aerosols and reactive gases	Chamberlain, 1953, Fisher, 1975; Scriven and Fisher, 1975, Engelmann 1968, Wangen and Williams, 1978.
2. Distributed Washout Coefficient	Material (Differential)	Irreversible Attachment	Below-cloud scavenging of size-distributed aerosols	Dana and Hales, 1976, Slinn, in press.
3. "Two-Stage" Nucleation-Accretion	Material (Differential)	Irreversible Attachment	Condensation-enhanced below-cloud scavenging of aerosols	Radke, et al, 1978; Slinn, in press.
4. Nonreactive Gas Scavenging	Material (Differential)	Reversible Attachment	Below-cloud scavenging of nonreactive gases	Hales, et al., 1973; Slinn, 1974; Barrie, 1978.
5. Reactive Gas Scavenging	Material (Differential)	Reversible Attachment with Aqueous-Phase Reaction	Below-cloud scavenging of reactive gases	Hill and Adamowitz, 1977; Overton, et al. 1979; Durham, et al. 1981; Adamowitz, 1979; Drewes and Hales, in press.
6. In-Cloud Aerosol Scavenging	Material (Differential)	Irreversible Attachment	Scavenging in storm systems (nonreactive)	Klett, 1977; Storebo and Dingle, 1974; Dingle and Lee, 1973; Slinn, in press; Junge, 1963; Lange and Knox, 1977.
7. In-Cloud Aerosol Scavenging	Material (Integral)	Irreversible or Reversible Attachement	Scavenging in storm systems	Engelmann, 1971; Gatz, 1972; Scott, 1978; Slinn, in press; Hales and Dana, 1979.
8. In-Cloud Reactive Gas and Aerosol Scavenging	Material (Differential)	Transport, Reaction and Deposition	Scoping studies	Omstedt and Rodhe, 1978; Gravenhorst, et al. 1975.
9. In-Cloud Reactive Gas and Aerosol Scavenging	Material (Integral)	Irreversible or Reversible Attachment with Chemical Reaction	Interpretation of field study data	Scott, in press.

continued...

Table 2. Concluded.

Model	Type of Balance Equation(s)	Mechanism(s)	Typical Application	Pertinent References
10. **Composite Analytical**	Material (Differential)	Transport, Reaction and Deposition	Regional scale deposition	Fay and Rosenzweig, 1980; Astraita and Wei, 1979.
11. **Composite Trajectory**	Material (Differential)	Transport, Reaction and Deposition	Regional scale deposition	Heffter, 1980; Kleinman, et al. 1980; Shannon, 1981; McNaughton, et al. 1981; Bhumralkar, et al. 1980; Bolin and Persson, 1975; Hemmi, 1980; Hales, et al. 1977; Sampson, 1980; Bass, 1980; Voldner, et al. in press; Eliassen, 1978; Fisher, 1978; Patterson, et al. 1981.
12. **Composite Grid**	Material (Differential)	Transport, Reaction and Deposition	Regional scale deposition	Liu, et al. 1977; Lavery, et al. 1980; Carmichael, 1981; Prahm, et al. 1977; Lamb, in press; Wilkening and Ragland, 1978; Lee, 1981.
13. **Composite Statistical**	Material	Transport, Reaction and Deposition	Scoping studies and lifetime assessment	Rodhe and Grandell, 1972.
14. **Nonreactive**	Material Energy and Momentum (Differential)	Irreversible Attachment, Nonreactive	In-cloud scavenging analysis	Hane, 1978; Molenkamp, 1974; Kreitzburg, et al. 1978.
15. **Reactive**	Material and Energy (Differential)	All modes of scavenging, including chemical reaction	In-cloud scavenging analysis	Hales, in press.

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SESSION I

AIR

THE DESIGN OF AIR QUALITY MODELS FOR ECOLOGICAL IMPACT ASSESSMENT

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Abstract

The assessment of ecological impacts requires different information from an air quality model than is required for existing air quality regulations. A user survey undertaken for AOSERP indicated that four concepts should be considered for an effective air quality model:

1. The susceptibility of receptors as functions of ambient meteorological conditions.
2. The susceptibility of receptors as function of exposure time.
3. The recovery concept.
4. Deposition, location and migration.

A climatological frequency distribution model was built for the Research Management Division (RMD) of Alberta Environment which included the first three of the above concepts; a separate, small-scale model is necessary for the fourth. The structure of the new model permits much more flexible and careful studies of possible ecological impacts and is compared to the structure of the more familiar Climatological Dispersion Model (CDM).

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1. INTRODUCTION

An air quality model for ecological impact assessment has different design specifications than a model for maintenance of air quality regulations. The Research Management Division of Alberta Environment, having recognized the specific information requirements of these respective applications, has sponsored work over the past three years to develop accommodating models.

2. AIR QUALITY REGULATIONS AND WORST-CASE MODELS

Air quality regulations vary somewhat among the Canadian jurisdictions, but basically follow the federal air quality guidelines. These guidelines define a series of ground level concentrations (GLC) averaged over varying time periods. These GLC values should not be exceeded more than once per year. A sample of these guidelines for SO_2 is shown in Figure 1.

Air quality models which attempt to estimate worst-case GLC values can be used for regulatory purposes. Such an application has two types of limitations. The definition of a worst case, its predictions and its detection are all difficult to achieve reliably and, secondly, the regulations themselves are not adequate measures of ecological impact.

The use of the worst case or second worst case in one year mean that the regulations are attempting to define extreme values. Monitoring networks may not resolve spatially limited extreme values and so monitor placement becomes very sensitive.

A more fundamental problem, however, is associated with the statistics of extreme values. Air quality models usually predict the ensemble mean for given conditions. The plume sigma formulation presented by Pasquill (1976), for example, and now recommended by the AMS (Hanna et al. 1977) represents an ensemble mean of data with considerable scatter. Models generally utilize such results and so are not designed to handle extreme cases.

In spite of these limitations, worst case models have proved useful for the implementation of air quality guidelines by regulatory agencies. The guidelines are meant to provide a base level of air

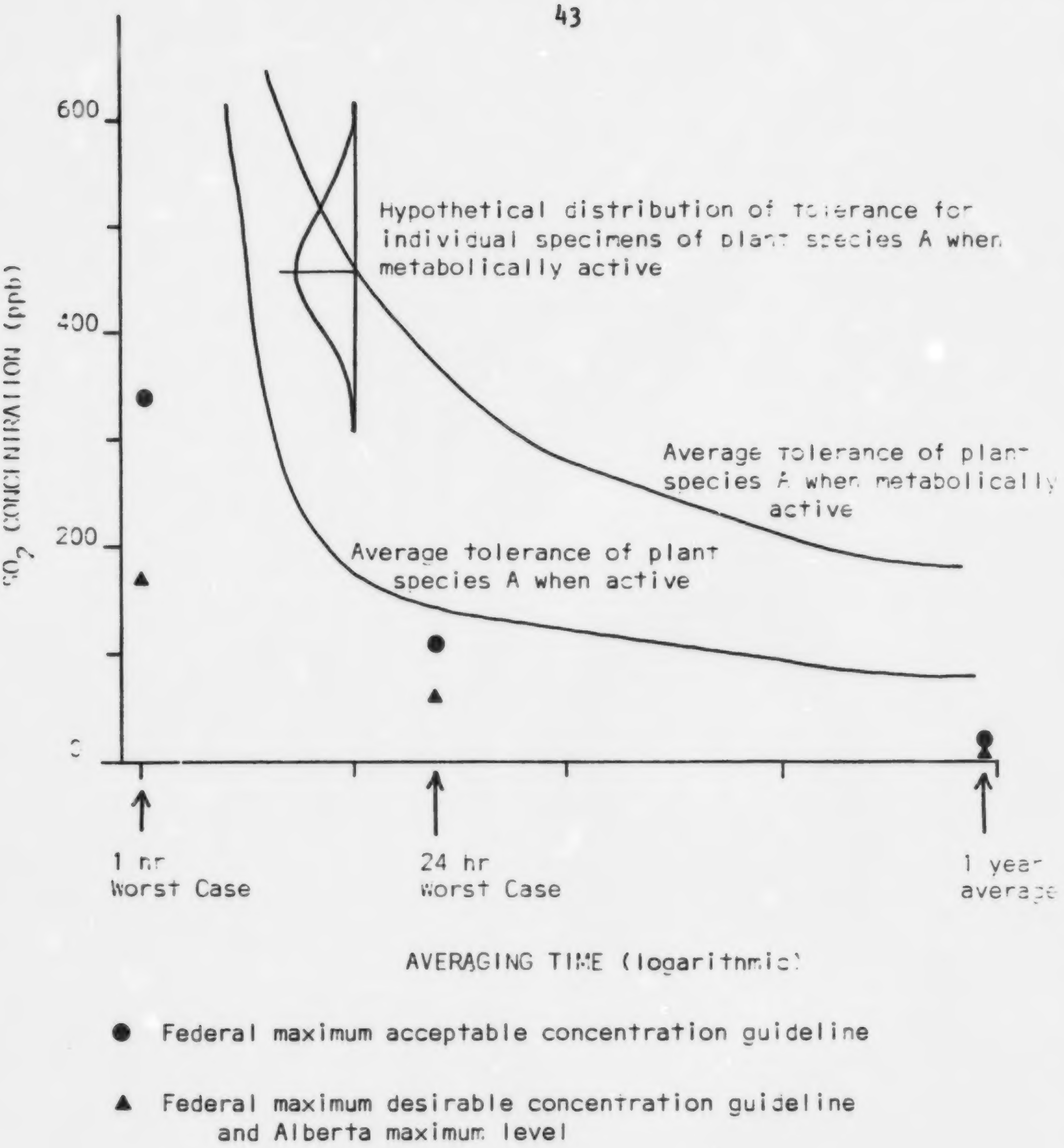

Figure 1. A sketch of the tolerances of hypothetical plant species A and B to SO_2 while metabolically active. The concepts illustrated are that different species will have differently shaped tolerance curves and that individual specimens within a species may respond differently. Air quality models that predict only one-hour worst-case values may be completely inadequate for impact assessments.

quality below which ecological damage or significant nuisance effects will not occur. However, exceedances of the guidelines may not necessarily cause ecological problems. Assessing air pollutant impacts requires more statistical and climatological information than is available from worst-case air quality models.

3. ASSESSMENT OF ECOLOGICAL IMPACTS

In conjunction with AOSERP, a user survey was undertaken (Davison and Lantz 1980) in an attempt to abstract the relevant biological concepts into design specifications for a climatological air quality model. There were four major concepts arising from the user survey:

1. the susceptibility of receptors as a function of ambient meteorological conditions;
2. the susceptibility of receptors as a function of averaging time or exposure time;
3. the recovery concept; and
4. deposition, location and mitigation.

Many of the major components of the ecosystem have varying levels of susceptibility to GLC depending upon season, time of day, temperature, etc. For example, trees exposed to a high level of SO_2 during cold weather and slight solar radiation in the water may be totally unaffected; whereas, that same concentration on a warm June morning might cause serious damage. Thus GLC values need to be linked to ambient conditions in order to evaluate their ecological impact.

Receptors generally have a susceptibility that varies with the duration of the exposure (i.e., averaging time). Some highly schematic examples are sketched in Figure 1. Note that different species will have different average sensitivity curves. Different individuals within a species will have different curves, depending upon ambient conditions and the strength and age of the individual. Furthermore, these curves may exhibit a very different shape from that of the regulatory limits. A model disigned for impact assessment thus needs the capacity of simulating probabilities of GLC values for various averaging periods in order to relate to sensitivity curves of various species.

The recovery concept was emphasized by each of the biologists interviewed in the user survey. If a plant has been exposed to high GLC values and has suffered some damage, then it may be able to fully recover, provided that exposure is not repeated during this recovery period. The time that elapses between episodes is therefore important. A model should have the capability to provide time-domain statistics, such as the frequency distribution of time between GLC episodes.

The location of the deposition and migration of any acidic component is a further area of concern. The detailed location of that deposition on the canopy, on the tree tunnels, on the forest litter, on the open fen areas or open water involves a detailed surface specification. If deposition occurs on snow, then the majority of the acidic ions may be reached from the snow during melt and flushed into the water system. Dispersion models can provide estimates of GLC values at canopy top and rough estimates of total deposition. Detailed deposition and ion transport of the deposited material is, however, best handled in a separate model driven by data from the dispersion model.

4. DESIGN OF THE RMD FREQUENCY DISTRIBUTION MODEL

4.1 PROJECT OUTLINE

The previous sections outlined some of the design specifications for an air quality model to be used as a tool in assessment of ecological impacts. INTERA has developed such a model on behalf of RMD of Alberta Environment.

The model includes a dispersion formulation which incorporates the results of many of the AOSERP field studies and is consistent with the boundary layer similarity theory. The data base to drive the model and the model validation studies were developed jointly by Western Research and INTERA. The design features of the model relevant to the use for assessment of ecological impacts are described below. The details of the model and data base have been presented in reports to Alberta Environment (Davison et al. 1981 a,b,c, and Leahey and Hanson 1980).

4.2 DESIGN SPECIFICATIONS AND A GLC TIME SERIES

The design specifications discussed above indicated the need for a file containing a time series of predicted GLC values with the associated ambient meteorological conditions as a basis for further analysis. Historical meteorological data could be used to drive a dispersion model to generate this file with any desired operational scenario as the emission sources. The following discussion outlines how the four major concepts from the user survey are satisfied by the model-generated time series of GLC values.

The susceptibility of receptors to ambient conditions can be simulated by weighting the GLC values depending upon existing meteorological conditions to generate effective GLC values.

$$GLC_{eff} = (WP) * GLC_{pred}$$

where

GLC_{eff} is the effective GLC value

GLC_{pred} is the GLC value predicted for the given meteorological condition

WP is a weighting parameter which is a user-defined function of ambient meteorological conditions.

The use of weighting parameters becomes clearer with an example. Suppose that a user is interested in the effects of some gaseous emission on a particular species of tree and knows that the tree is relatively insensitive to GLC values when the temperature is below freezing. The tree then becomes progressively more sensitive to higher temperatures until at 20°C, the stomata are fully open and no increased sensitivity occurs. The weighting parameter could be set to 0.0 at 0°C, 1.0 at 20°C and made a linear function of temperature between 0°C and 20°C. The effective GLC time series for this species of tree would then consist of zeros whenever the temperature was less than 0°C and consist of increasing fractions of the normally predicted GLC value for higher temperatures.

The user can define weighting parameters to be simultaneous functions of any parameters on the time series file (e.g., temperature, solar radiation, relative humidity, time of day, season, rainfall, etc.). Thus, a biologically oriented user can use the weighting parameters to generate a time series of GLC values that reflects a receptor's susceptibility; this time series of effective GLC values can then be statistically analyzed for any developmental scenario desired.

The second design specification concerns the susceptibility of receptors as a function of exposure time. With a time series of hourly averaged GLC values, compression of the data into other user-defined averaging times for subsequent analysis is easily provided for in the model.

The details of deposition and migration of acidic components of deposited materials are best examined by a separate model. The air quality model provides a time series file of predicted GLC values at various receptor locations for input to such a deposition and ion transport model. Initial estimates of wet and dry deposition for indications of the general magnitude of the problem are made using deposition velocities.

4.3 MODEL STRUCTURE

A problem in generating a time series of GLC values is that a large amount of computer time and hence a large budget may be required. The RMD model was designed to minimize computer costs by using a two-stage approach, as outlined in Figure 2.

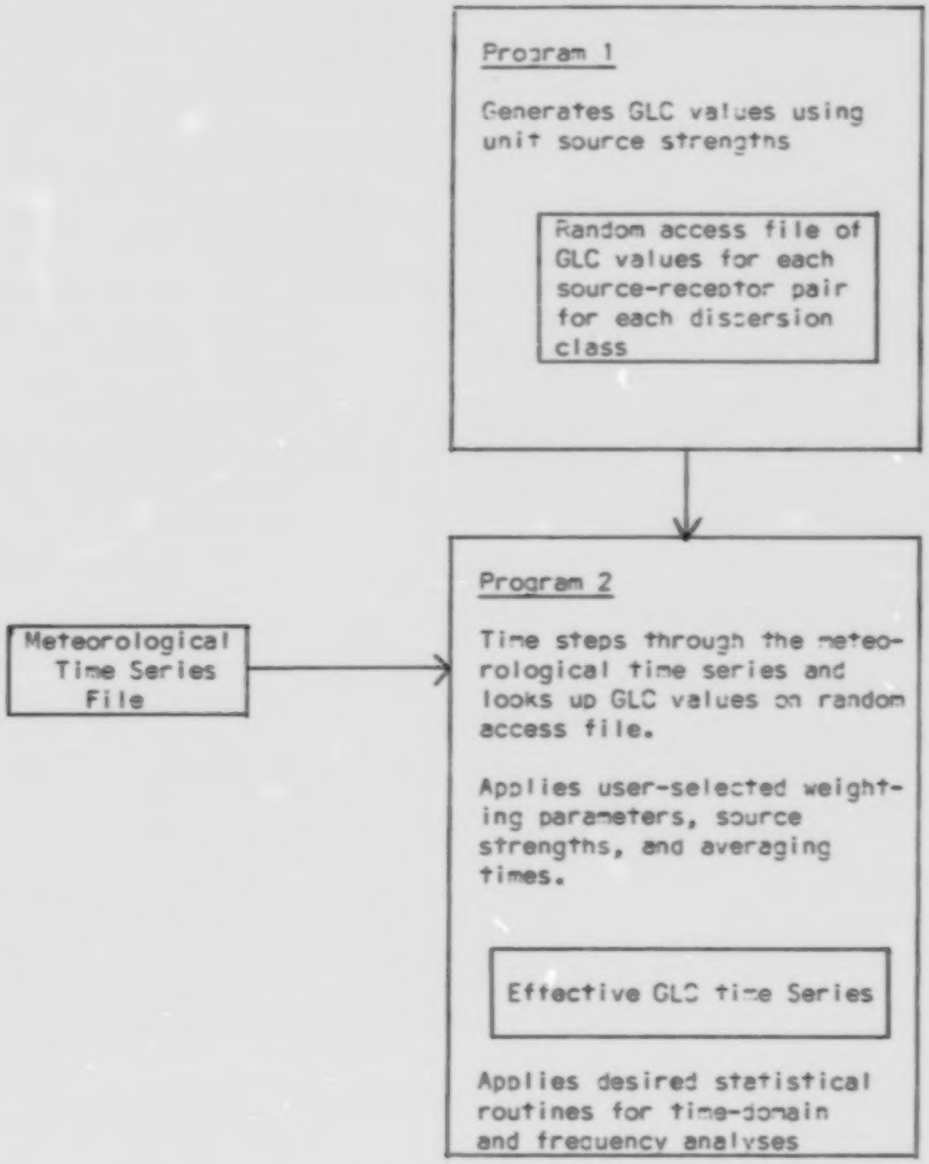
Program 1
Generates GLC values using unit source strengths
Random access file of GLC values for each source-receptor pair for each dispersion class
Program 2
Time steps through the meteorological time series and looks up GLC values on random access file.
Applies user-selected weighting parameters, source strengths, and averaging times.
Effective GLC time Series
Applies desired statistical routines for time-domain and frequency analyses
Meteorological Time Series File

Figure 2. A schematic summary of the structure of the RMC climatological frequency distribution model developed by INTERA.

The first program generates a matrix of GLC values as functions of discretized meteorological dispersion parameters (wind speed, wind direction, corrective mixing height and surfact heat flux). The GLC values for each source-receptor pair using unity source strengths are stored in a random access file.

The second program reads a time series file of meteorological conditions and calculates a dispersion index from the dispersion parameters which corresponds to the appropriate storage location on the GLC random access file. Source strengths are user-defined in the second program so that sources can be turned off or on to study the contributions of various emitted species from the various sources at a given receptor. This second program then generates the GLC time series file which can be modified by weighting parameters and analyzed as desired.

4.4 COMPARISON OF THE RMD MODEL STRUCTURE WITH THE CDM

The structure of the present model can be contrasted with the structure of the traditional CDM. In the latter, the GLC matrix is calculated for the various dispersion classes; the meteorological data are analyzed into a frequency distribution of dispersion classes; then, the frequency distribution of GLC values is calculated by multiplying the corresponding elements of the two matrices (see Figure 3). Note that the time relationships between events are lost when the meteorological data are transformed into a frequency distribution. Thus, time between episodes and durations of exposure cannot be studied. The variation of the susceptibility of receptors is not considered and different emission scenarios or seasonal dependences can be studied only by re-running the entire model.

In contrast, the GLC matrix in the RMD model needs to be generated only once. Source variation, various susceptibility functions and various averaging periods can then be run using the second program and the random access file of GLC values. The RMD model provides a more flexible and effective tool for impact assessment than has been available to date.

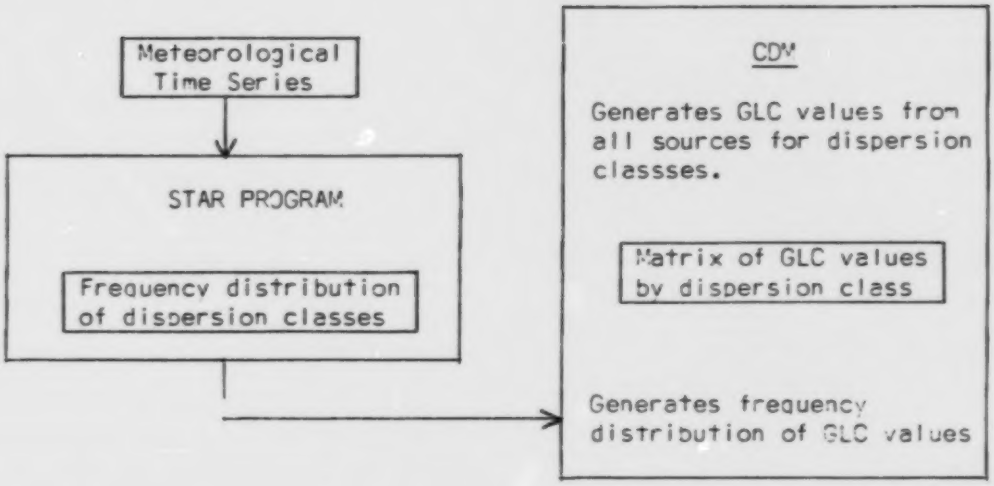
Meteorological Time Series
STAR PROGRAM
Frequency distribution of dispersion classes
CDM
Generates GLC values from all sources for dispersion classses.
Matrix of GLC values by dispersion class
Generates frequency distribution of GLC values

Figure 3. A schematic summary of the structure of the CDM for comparison with the RMD model.

A difficult problem now remaining is how to ensure that those scientists and planners examining potential environmental impacts effectively use the tools, such as this new RMD model, that dispersion meteorologists and other physical scientists provide.

5. CONCLUSIONS

This study leads to the following conclusions:

1. An air qulaity model for assessment of ecological impacts has different design specifications than a model for maintenance of air quality regulations.
2. Four concepts of importance for impact assessment are: (1) the susceptibility of receptors as a function of meteorological conditions; (2) the susceptibility of receptors as a function of exposure time; (3) the recovery concept; and (4) deposition, location and migration.
3. A climatological frequency distribution model developed by INTERA for RMD of Alberta Environment is designed to be a more effective tool for impact assessment than conventional models designed for regulatory applications or existing climatological dispersion models.

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POTENTIAL SULPHUR LOADING IN WESTERN CANADA DUE TO OIL SANDS EXTRACTION PLANTS

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W.A. MURRAY[2], S. DJURFORS[3]

ABSTRACT

The projected development of the Alberta oil sands over the coming decades will produce a two-fold increase in total sulphur emissions in northern Alberta. In order to determine the long-range transport impact of these emissions, the Oil Sands Environmental Study Group initiated a modelling assessment study to examine the total impact of emissions over the 50-year period from 1967 to 2017 as the new extraction plants come on stream.

The Meteorological and Environmental Planning Limited TRANS model has been used to determine the long-range transport and environmental loading of sulphur and nitrogen compounds using a detailed emissions inventory and projected inventory for the Tar Sands. In order to generate a realistic 50-year loading estimate, a representative year was selected to correspond as closely as possible to the long-term climatology of the Prairie provinces. Seasonal evaluations were then carried out for each of the 50 years using the representative year, treating each source separately, and combining the results.

This paper details the methodology and presents some results of the evaluation.

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1. INTRODUCTION

The Alberta Oil Sands development program is expected to add another 10 oil extraction plants by the turn of the century, situated primarily in the Tar Sands and Cold Lake regions. This development will be accompanied by an increase in the emissions of sulphur and nitrogen oxides to the atmosphere and will lead to increased loadings of sulphur and nitrogen to the aquatic and terrestrial components of the ecosystem.

As part of an overall program designed to document the effect of the Oil Sands Development on the ecology of the region as the development proceeds, the Oil Sands Environmental Study Group (OSESG) initiated a study of the long-range transport of the sulphur and nitrogen oxide emissions originating from the currently operational and the projected oil extraction plants. The study carried out by Meteorological and Environmental Planning Limited (MEP) was designed to delineate the transport and deposition of the sulphur and nitrogen oxide emissions by modelling the physical and chemical processes which carry the emitted pollutants to the several compartments of the ecosystem.

The results of the study provide an estimate of the amount of primary emissions as well as the secondary products which are input to the terrestrial or aquatic ecosystem on a regional basis within Alberta and surrounding regions. Such an estimate is required for the region due to the lack of sufficient monitoring data to define the level of loadings being experienced by the ecosystem, and is the only method by which projection of effects into the future can be made quantitatively.

In order to carry out such an assessment, the following components are essential:

1. Generation of a projected emissions inventory for the period being studied;
2. Selection of a meteorological period which would be representative of the long-term;
3. Evaluation of the environmental loadings by use of a mathematical model.

The projected emissions and selection of typical meteorology are essential to the capability of making predictions over the entire period 1967 to 2017 with sufficient confidence.

The evaluation of loadings was carried out using the TRANS model which has been used by MEP to evaluate regional sulphur and nitrogen transport in eastern North America. The performance of the model with the total Eastern North American Emissions Inventory has been evaluated against monitored data over a one-year period, and shown to reproduce the regional deposition fields in a realistic fashion.

2. CURRENT AND PROJECTED EMISSIONS SOURCES

2.1 METHODOLOGY OF EMISSIONS PROJECTIONS

Severl sources of information were used to produce a composite inventory. For the historic emissions for the period 1967 through 1981, the existing plant operations, Suncor and Syncrude, provided the necessary data on sulphur and nitrogen oxides emissions and the emissions conditions. The historical data also provides the basis for defining the typical rate at which a new plant would come on-stream and the variation in emissions during the commissioning period, which is estimated to be approximately six years.

The existing operations also provide a model of the typical NO_x emissions and the primary sulphate emissions for the projected plants. It is recognized that as new plants are built with changing technology, they are likely to depart from the assumed model in terms of proportion of NO_x to SO_2 emissions and primary sulphate emissions. However, it is expected that the model used provides a worst case operating configuration for the future plants, and should therefore provide a conservative estimate of future emissions (i.e., tend to over estimate future emissions).

For the planned extraction plants, Alsands, and Cold Lake (Esso), projected emissions of SO_2 were extracted from the EIA submissions, while NO_x emissions were estimated using the model of existing plants. The start-up of these plants has been moved back to 1988 and 1990 respectively.

Beyond the planned extraction plants, the assumption is made that a new plant would be phased in every third year, to be located in one of the regions of Athabasca, Cold Lake and Wabasca. A total of nine such plants would be started up by the year 2017.

2.2 EMISSIONS INVENTORY FOR PERIOD 1967 TO 2017

The sulphur dioxide emissions from current and projected extraction plants are displayed graphically in Figure 1. For each year in the period 1967 to 2017, the individual plant contributions are graphically added to produce the total emissions. The numbers within the histogram identify the source as listed in Table 1. The table also lists the known or projected location of the plants. The distribution of these plants can be seen readily in Figure 2.

The peak total emissions from oil sands development are projected to reach 185 kT sulphur per year in the year 2012, falling off the following year as the Syncrude plant shuts down. In 2017, the annual rate of emissions is 160 kT S, or approximately two times the 1980 emissions. These are, however, dispersed over a much broader area.

The primary sulphate emissions are assumed to be 1% of the $S0_2$ emissions for all plants; the maximum emission rate is then 3.7 kT sulphate per year in 2012.

The $N0_x$ emissions are displayed in Figure 3. For projected plants, the $N0_2$ emissions are assumed to be 20% of the $S0_2$ emissions, this being the average of the Suncor and Syncrude present operations. The 2017 emissions of $N0_2$ are approximately 80 kT/y, evenly distributed among the 11 plants in operation.

By way of comparison, the sulphur emissions from Oil Sands extraction can be compared to total sulphur emissions from Alberta. From 1978, total emissions of sulphur were approximately 260 kT/y. The Oil Sands plants contributed about 20% of ths total. If the other contributions to emissions do not change over the next forty years, total sulphur emissions for Alberta will amount to 385 kT S/y. The Oil Sands contribution to the total will amount to 50%.

Table 1. Current and projected sources, Alberta Oil Sands development.

Source	Sponsor	Startup Date	Location Lat.	Location Long.
1	Suncor	1967	57° 00'	111° 28'
2	Syncrude	1978	57° 02'	111° 35'
3	Syncrude Expansion	1988	57° 02'	111° 35'
4	Alsands	1988	57° 17'	111° 30'
5	Cold Lake	1990	54° 37'	110° 30'
6	Canstar	1993	57° 25'	111° 33'
7	Sandalta	1996	57° 11'	111° 25'
8	Cold Lake Expansion	1999	54° 37'	110° 30'
9	Texaco	2002	57° 05'	111° 05'
10	Shell Peace River	2005	56° 25'	116° 45'
11	Wabasca	2008	55° 59'	113° 10'
12	Amoco	2011	56° 28'	111° 05'
13	Cold Lake B	2014	54° 43'	110° 05'
14	Surmont	2017	56° 06'	110° 52'

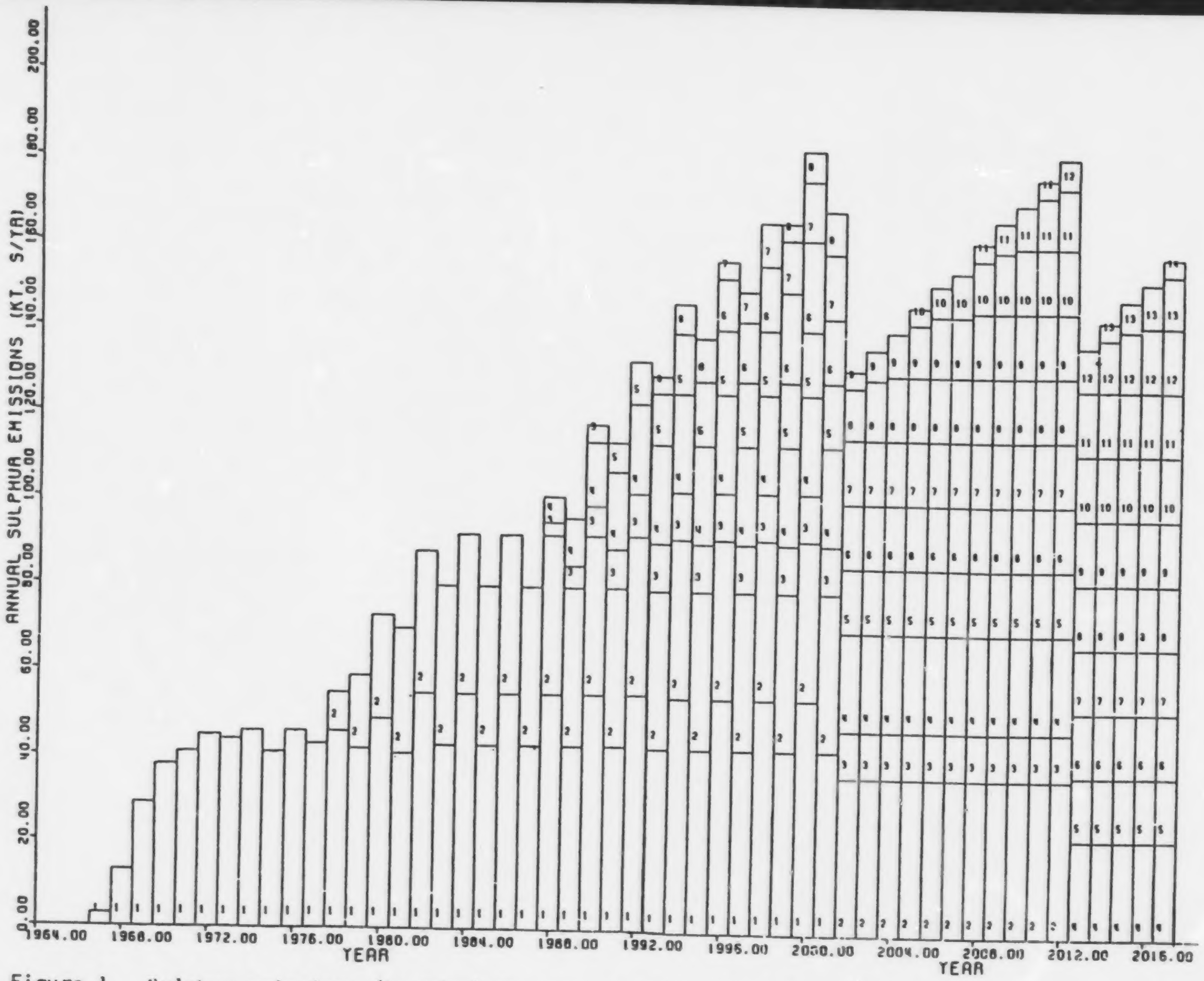

Figure 1. Sulphur emissions (kt S/yr) for period 1967 - 2017 from Alberta Oil Sands Plants.

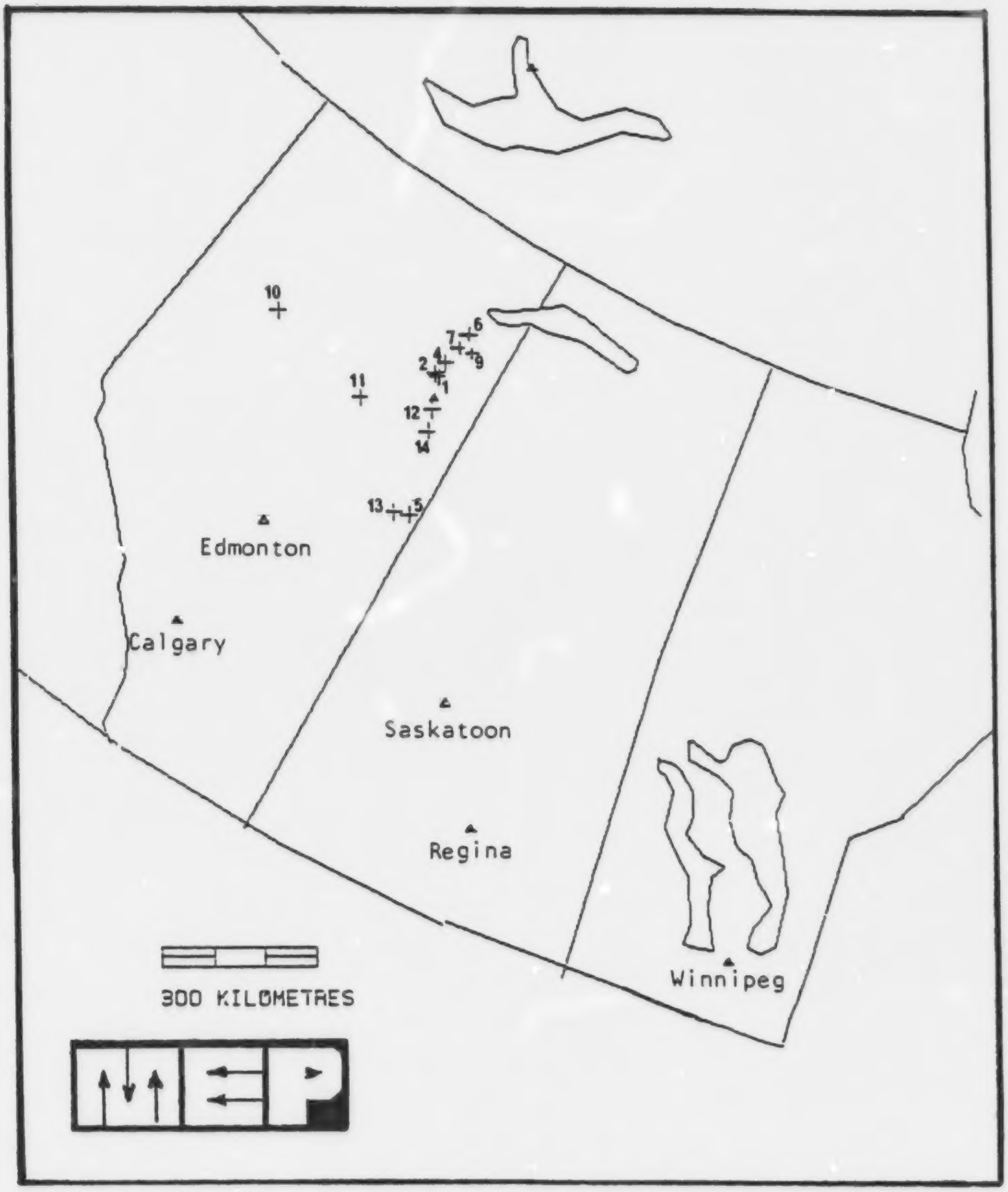
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Figure 2. Location of current and projected sources for Oil Sands development.

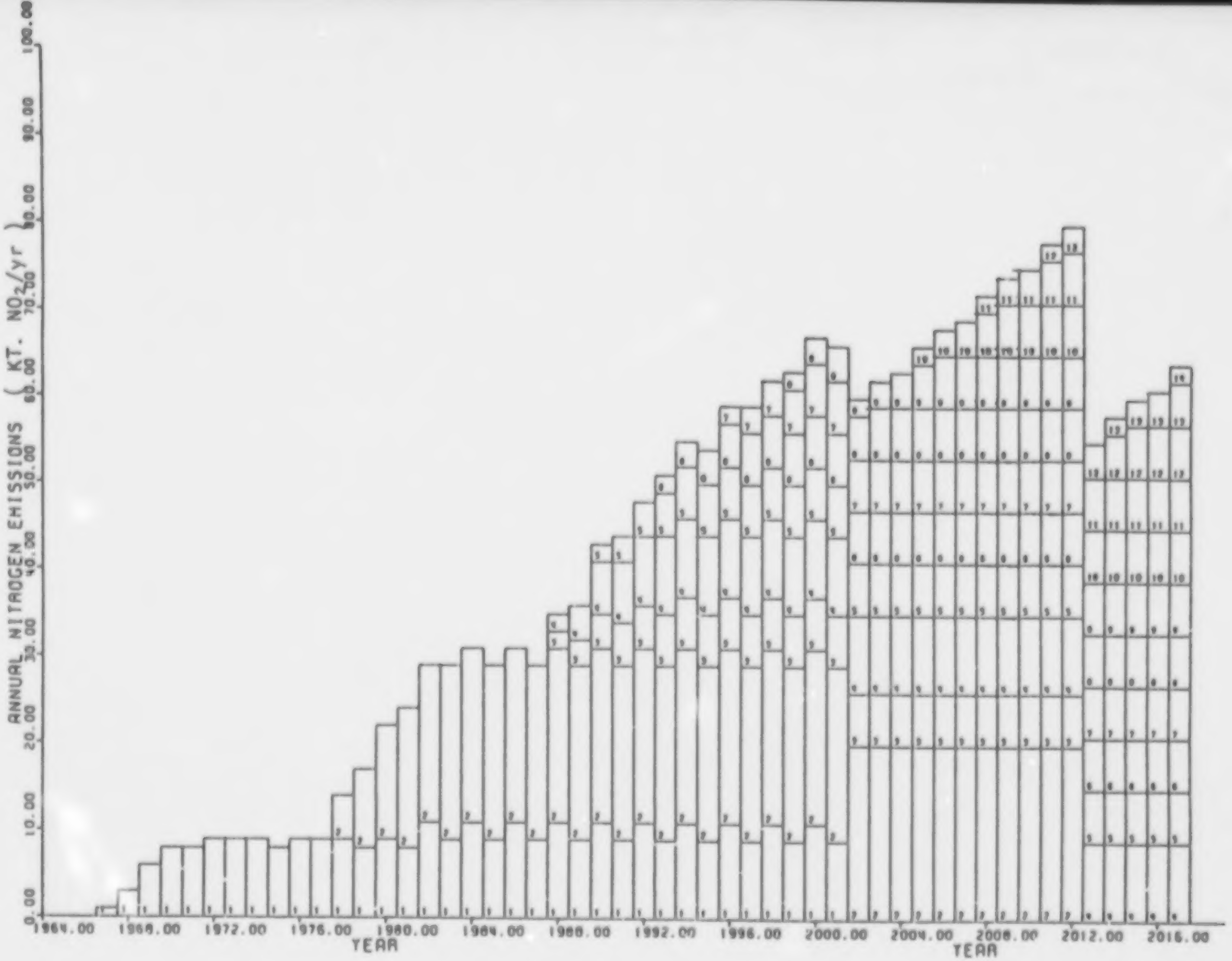


Figure 3. Nitrogen emissions (kT NO_2/yr) for period 1967 - 2017 from Alberta Oil Sands plants.

3. LONG-RANGE TRANSPORT OF SULPHUR AND NITROGEN COMPOUNDS

3.1 TRANS MODEL DESCRIPTION

The evaluation of loadings was carried out using the TRANS model (Weisman 1981). The TRANS model is a trajectory-based model which treats the transport and dispersion of individual source plumes. Each plume is assumed to be transported within a two-dimensional wind field and diffused in the vertical and lateral dimensions.

Transport winds are derived from archived gridded fields of mean sea level pressure distributions using the geostrophic approximation and making an adjustment to speed and direction to produce winds representative of the transport layer.

Lateral dispersion about the plume centerline is Gaussian with empirically defined spread parameters. Vertical diffusion is uniform within each of four layers, with material cycled between the layers as the mixing height varies during the day. Thus, at a given time, some of the material is trapped within the mixed level, with the balance being transported above this level.

Material is dry-deposited from the surface layer only, using a bulk parameterization through the deposition velocity concept. This process is assumed to undergo a diurnal cycle similar to that of the build-up and decay of the mixing level, and also exhibits a seasonal cycle to reflect changes in the surface uptake characteristics.

Transformation of SO_2 to SO_4, and NO_2 to NO_3, is assumed to follow a first order process with a rate which follows diurnal and seasonal cycles reflecting the variation in photochemical activity. The conversion of NO to NO_2 is assumed to be instantaneous within the model.

Wet removal of particulate sulphur and nitrogen, as well as NO_2, is treated through the scavenging coefficient concept. The removal efficiency is dependent on the precipitation rate and type, and is determined empirically. The wet removal of SO_2 is assumed to depend as well on the mean pH of the rain, to account for the reversible nature of SO_2 sorption by the raindrop (Barrie 1981).

The model calculates the resulting concentrations and wet and dry depositions for each source from the predetermined plume positions at three-hourly intervals. The plume content of sulphur and nitrogen species is updated at three-hourly intervals to reflect the removal mechanisms. The three-hourly values are calculated at each of the receptor points of interest and the results averaged for the desired time intervals.

The output from the model consists of concentrations and wet and dry depositions at the specified receptor points for each source and for the four species.

3.2 METHOD OF APPLICATION FOR OIL SANDS SOURCES

3.2.1 Emissions Data

The emissions data and projections compiled as described in Section 2 form the basis for the historical and projected concentration and loadings estimates. Due to the linearity of the model, both for dispersion and chemistry, loadings are proportional to emission rate and multiple source contributions are additive. This permits generation of loadings for modified emissions from a given source by scaling of the model output values. Thus, a total of 12 different source configurations were calculated in full detail using the model, and then scaled according to the projected emissions inventory.

3.2.2 Trajectory Calculations

Trajectories were calculated originating from each of the 12 locations at three-hourly intervals and tracked for five days' duration (at maximum) for a full year. The year 1968 meteorological data were used to determine the trajectories, the same trajectories then being used for all years modelled. This year was found to represent the long-term climatology most closely, as detailed in Section 4, and serves as a representative year on which to base future long-term projections.

3.2.3 Calculations of Concentrations and Loadings

Using the 1968 three-hourly trajectories and the actual 1968 precipitation, the dispersion model was run for the full year for unit emissions from each of the 12 source points. Using the 50-year emissions inventory, a combined value for concentration and loading was determined for each year at the receptor locations indicated in Figure 4 by scaling each source to the appropriate emissions value. The receptors were selected at present monitoring sites, population centres, ecologically sensitive areas, as well as to provide sufficient density for mapping purposes.

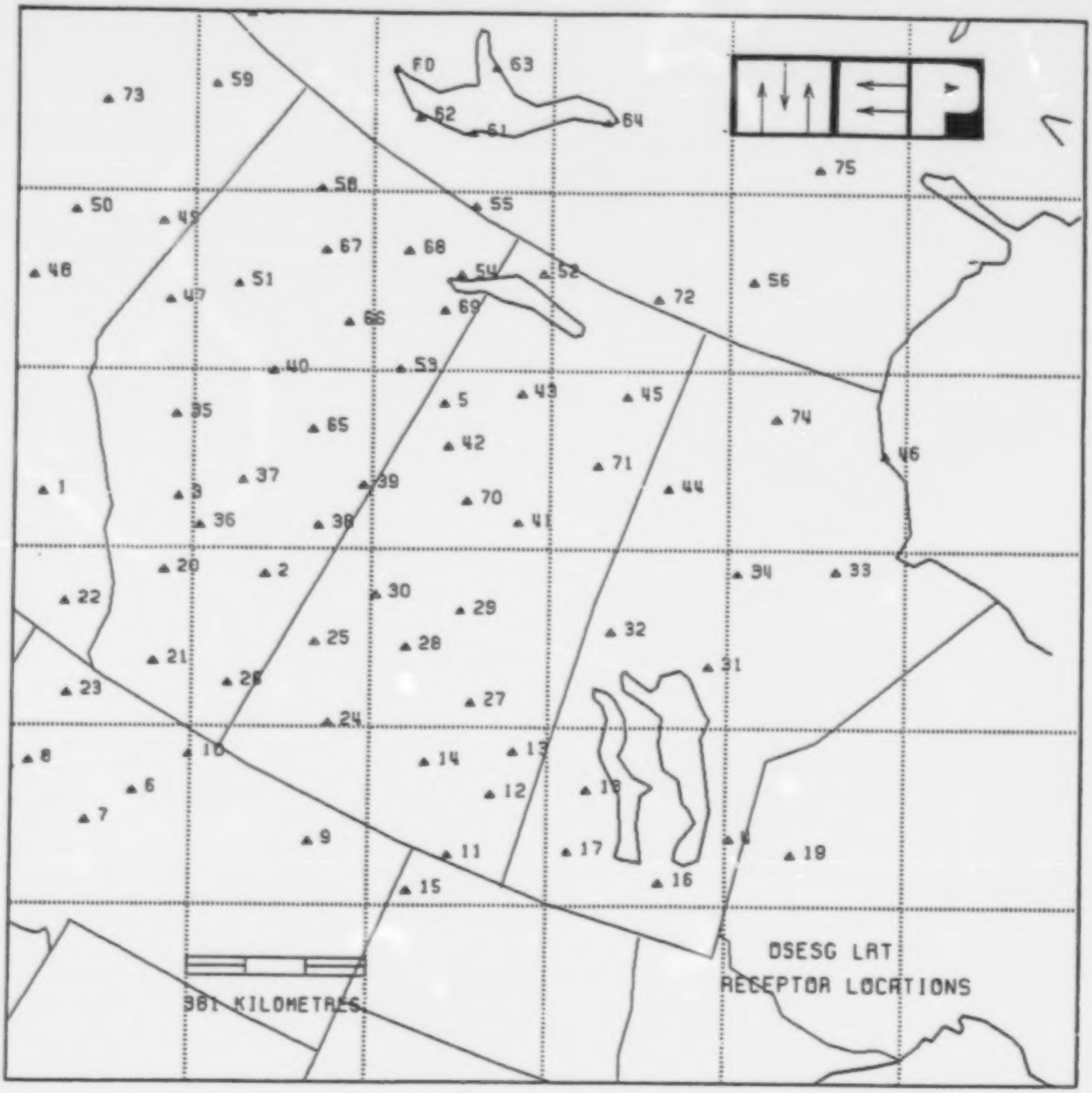
The transformation and removal parameters used for the simulation are listed in Table 2. These are based on literature values and the experience with predictions carried out for eastern North America. The reduced value of oxidation rate for SO_2 is chosen to reflect experimental data in the Tar Sands area (Barrie et al. 1978). Similarly, the dry deposition of SO_2 to snow-covered surfaces has been found to be low (Barrie and Walmsley 1978).

Because the model uses seasonally averaged values for the parameters (plus diurnal variation where appropriate), and there is no local data which can be used to define these parameters more precisely, the sensitivity of the model predictions to variations in the model parameters was also determined to allow estimation of the potential errors in the predictions.

4. REPRESENTATIVE METEOROLOGY FOR LONG-TERM EVALUATION

The projection of environmental loadings over a 50-year period from projected emissions on the basis of actual climatological conditions requires the use of meteorological data which is representative of the long-term for the region. However, since the emissions configuration varies over the 50-year period, and since it is not possible to associate the appropriate meteorology with a given year's emissions in the future, it is necessary to keep the meteorology constant while changing the emissions configuration. In order for such a projection to be credible, the meteorology needs to be representative of the anticipated long-term conditions.

The one-year resolution of the emissions data and projections, and the large amount of computer time required for model runs, dictates that the model be run for a one-year period of meteorology. It is therefore, necessary to select a one-year meteorological period which is representative of the long-term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OSESG LRT
RECEPTOR LOCATIONS

Figure 4. Location of receptor points used in dispersion calculations.

Table 2. Transformation and removal parameters adopted for use in model simulations.

	Sulphur		Nitrogen	
	Summer	Winter	Summer	Winter
Primary Deposition Velocity (cm/s)	0.6	0.2	0.5	0.3
Secondary Deposition Velocity (cm/s)	0.1	0.1	0.1	0.1
Transformation Rate (% hr^{-1})	.5	.2	2.5	1.0
Primary Washout Rate (hr^{-1})	- *	-	0.1	0.1
Secondary Washout Rate (hr^{-1})	0.3	0.3	0.3	0.3

* Formulated in Terms of pH and Temperature

climatology of the area, and which will by extension be representative of the period 1967 to 2017.

In carrying out this selection, only those aspects which influence concentrations and loadings within the primary region of concern need to be considered.

These parameters are the transport winds and the precipitation pattern and characteristics. The selection of a representative year based on these parameters is discussed in this section.

4.1 DATA AVAILABLE

The definition of precipitation pattern and characteristics was based on total seasonal precipitation, the number of days in the season with significant precipitation, and the seasonal temperature means. To define the long-term climatology of these variables, a 30-year statistic as archived by the Canadian Climate Center was used. This data was available for a total of 42 stations covering the Prairie provinces, providing sufficient density to define the general patterns over the area of concern in the modelling.

To define the transport and dispersion patterns over the long-term, a 12-year record (1967 to 1978) of gridded pressure fields at three-hourly periods was used to calculate three-hourly trajectories of five days' duration from Fort McMurray. This 12-year record formed the candidate set for selection of a representative year.

Monthly mean data for precipitation and temperature was obtained for 52 stations for the 12-year period to use for comparison with the long-term climatology. For evaluation purposes, seasonal averages were produced for the precipitation and temperature fields. Two seasons were defined as: Summer--May through September; and Winter--October through April. Annual averages were also produced from the monthly data for comparison to the long-term means.

4.2 SELECTION PROCEDURE

4.2.1 Precipitation and Temperature Fields

The seasonal values of precipitation, number of days of precipitation, and temperature for each of the 12 candidate years were compared to the 30-year mean seasonal values by means of a spatial correlation coefficient.

In general, the temperature fields were very similar for the 12 years, correlations to the 30-year means being greater than 0.95 for each season and annually. Thus the temperature fields could not discriminate among the 12 years.

The correlation for total seasonal precipitation and number of days with significant precipitation was much more scattered, ranging from a low of 0.2 to a high of 0.97. This comparison singled out the years 1968 and 1971 as having by far the best correlation to the 30-year mean; the correlation coefficients showing the best comparison for annual means being shown in Table 3.

To further aid in the selection process, the data was plotted and machine contoured. Examination of the maps shows that 1968 was more representative of the 30-year mean than was 1971, and in fact, shows a remarkable resemblance to the long-term precipitation climatology.

4.2.2 Transport and Dispersion

For purposes of comparison of a given year to the 12-year mean, a statistic of transport and dispersion is required. This statistic is chosen to be the general distribution of air parcels originating from a given point.

To provide such a statistic, the grid within which the trajectories were calculated is divided into 38.1 km squares. Each hourly (interpolated) trajectory within a given season is then classified by the squares which it crosses at hourly intervals, and for each square a total is accumulated of the number of trajectory crossings within the season. The number of crossings can then be mapped as in Figures 5 and 6, which show the distribution of annual

Table 3. Correlation coefficients with the 30-year mean.

		Parameter		
		Temperature (Seasonal Mean)	Total Precipitation	Number of Days With Significant Precipitation
1968	Annual	.995	.969	.909
	Winter	.993	.642	.870
	Summer	.991	.742	.701
1971	Annual	.994	.970	.889
	Winter	.975	.724	.673
	Summer	.990	.686	.675

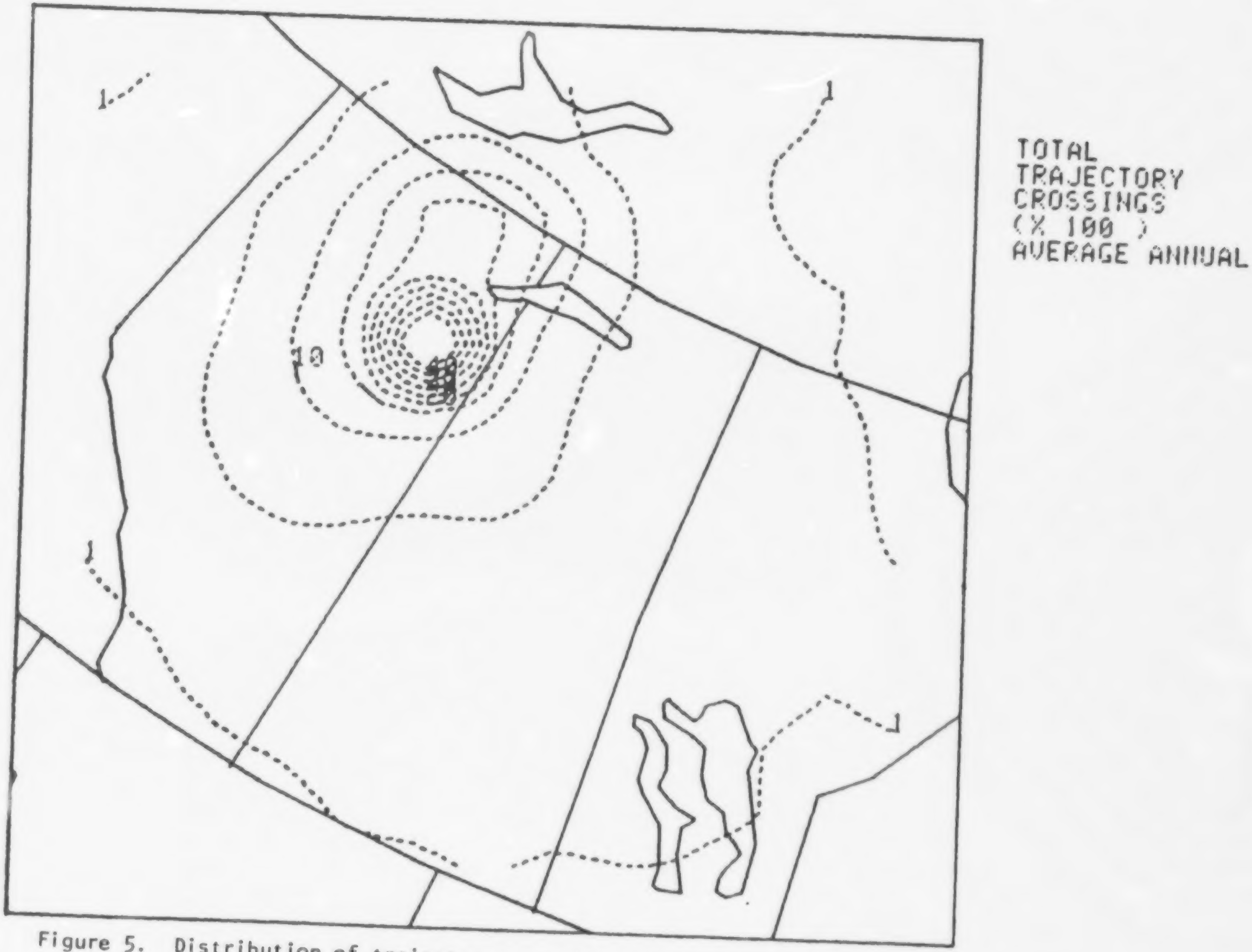
TOTAL
TRAJECTORY
CROSSINGS
(X 100)
AVERAGE ANNUAL
1
1
1
1
10

Figure 5. Distribution of trajectory crossing, average for 1967-1978.

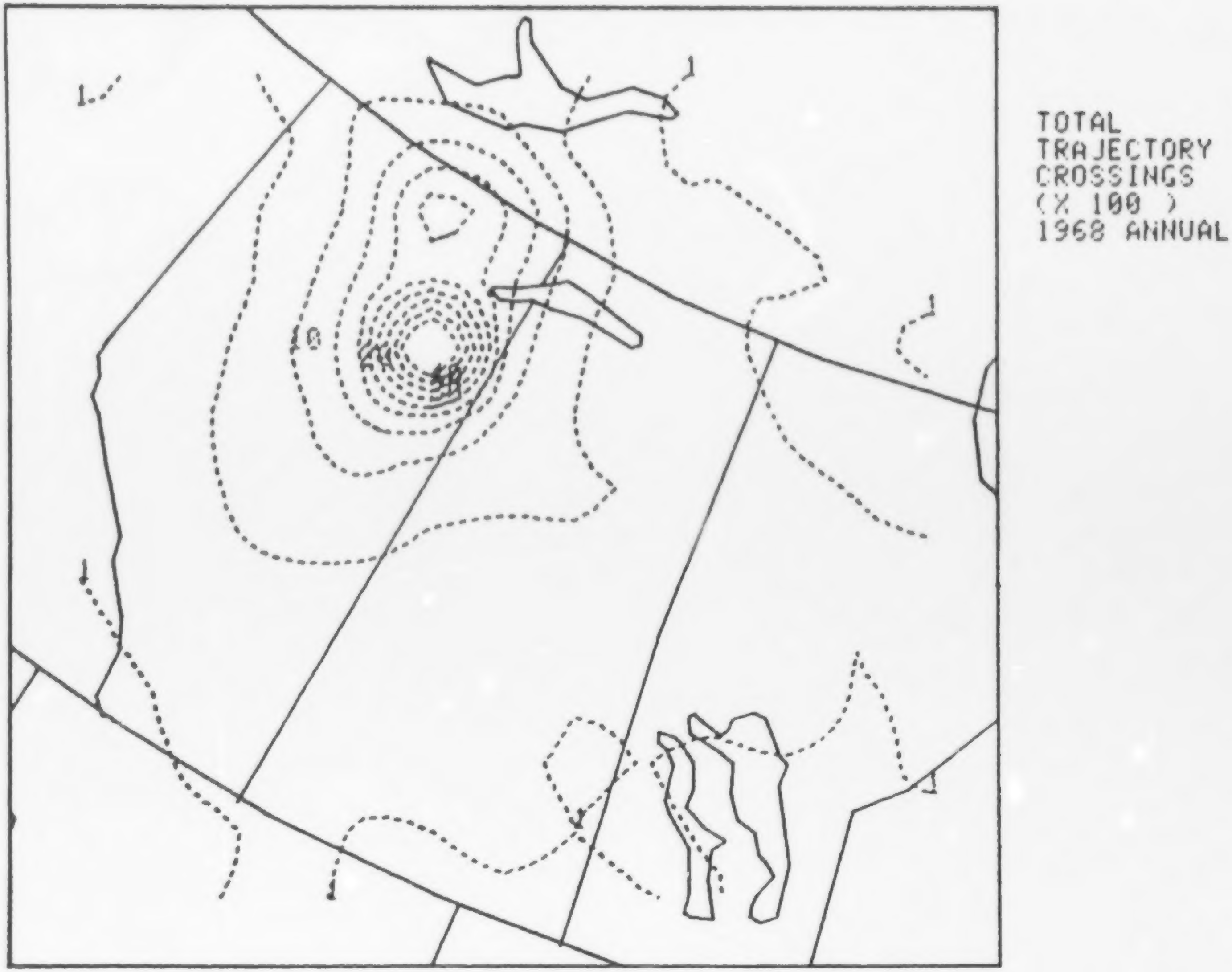
TOTAL
TRAJECTORY
CROSSINGS
(X 100)
1968 ANNUAL
1
1
1
1
1
1
1
10
24

Figure 6. Distribution of trajectory crossings, for 1968.

count of trajectory crossings for the 12-year average (Figure 5) and the 1968 annual total (Figure 6).

Comparison of the two patterns shows that these are very similar, even down to the level of 100 crossings per year.

It can be concluded that, with respect to the important parameters in the determination of loadings from the Oil Sands Development, 1968 provides a good basis for making long-term projections.

5. POTENTIAL CONTRIBUTION TO ENVIRONMENTAL LOADINGS

5.1 BASIS FOR EVALUATION

The evaluaton of the current and potential future contributions to environmental loadings of sulphur and nitrogen is based on the projected emissions as described in Section 2 for the period 1967 tp 2017.

The TRANS model was used to calculate concentrations and loadings for each source for a full meteorological record of one year, corresponding to 1968 actual data; this period was found to be representative of the long-term climatology for the western provinces as shown in Section 4. The use of a representative year should ensure that the projected results, if averaged over a number of years, are comparable to the actual loadings over the long term. For any one year, it is recognized that the use of 1968 data will not necessarily produce results closely resembling patterns of actual loadings.

The model parameters were chosen as described in Section 3, and have not been verified for the region of application. However, the sensitivity analysis of the model for annual predictions to the choice of parameters shows that such long-term averages are only moderately sensitive to the variation in parameter values.

5.2 PREDICTED LOADINGS OF SULPHUR AND NITROGEN COMPOUNDS

Tables 4 and 5 summarize the peak concentrations and loadings for the present (1980), the year 2017 and the average over the period 1967 to 2017.

Table 4. Comparison of sulphur concentrations and loadings at present with projected values in 2017 and the long-term mean. Values represent the maximum seasonal concentration or deposition attained at any receptor.

		Concentration ($\mu g/m^3$)		Wet Dep. kg/ha as S		Total Dep. kg/ha as S
		SO_2	SO_4	SO_2	SO_4	S
1980	Annual	4.2*	.21	1.3	.09	3.6
	Winter	4.5	.24	1.1	.03	1.9
	Summer	3.9	.19	0.3	.06	1.7
	Annual	4.8	.31	1.7	.12	4.3
	Winter	7.2	.40	1.1	.04	2.4
	Summer	2.5	.23	0.5	.08	1.8
Average 1967-2017	Annual	4.3	.25	1.5	.11	4.0
	Winter	5.0	.33	1.2	.04	2.2
	Summer	3.5	.21	0.3	.07	1.9

*Alberta annual average standard for SO_2 is 30 $\mu g/m^3$.

Table 5. Comparison of nitrogen concentrations and loadings at present and projected values in 2017 and the long-term mean. Values represent the maximum attained at a receptor.

		Concentrations ($\mu g/m^3$)		Wet Dep. kg/ha as N		Total Dep. kg/ha as N
		NO_2	NO_3	NO_2	NO_3	N
1980	Annual	.57	.09	.09	.03	.29
	Winter	.67	.11	.05	.02	.16
	Summer	.47	.09	.04	.01	.13
2017	Annual	.95	.19	.10	.05	.45
	Winter	1.45	.24	.05	.04	.29
	Summer	.44	.14	.05	.02	.17
50-Yr. Average	Annual	.71	.14	.11	.05	.44
	Winter	.92	.18	.06	.02	.25
	Summer	.51	.12	.05	.03	.19

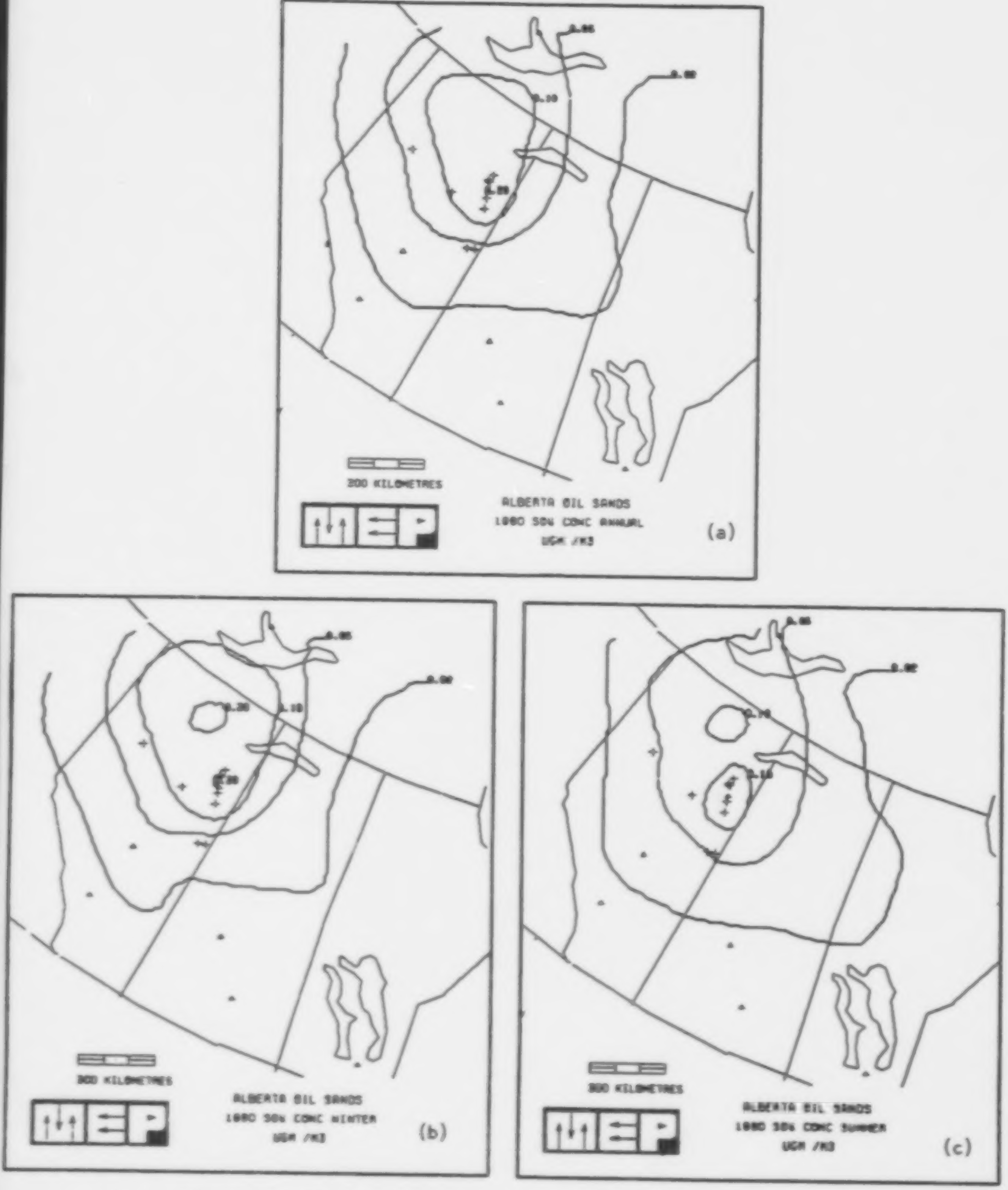
0.05
0.02
0.10
0.20
300 KILOMETRES
ALBERTA OIL SANDS
1980 SO4 CONC ANNUAL
UGM /M3
(a)
0.05
0.20
0.10
0.02
0.20
300 KILOMETRES
ALBERTA OIL SANDS
1980 SO4 CONC WINTER
UGM /M3
(b)
0.05
0.02
0.10
0.10
300 KILOMETRES
ALBERTA OIL SANDS
1980 SO4 CONC SUMMER
UGM /M3
(c)

Figure 7. Predicted 1981 SO_4 concentrations ($\mu g/m^3$).

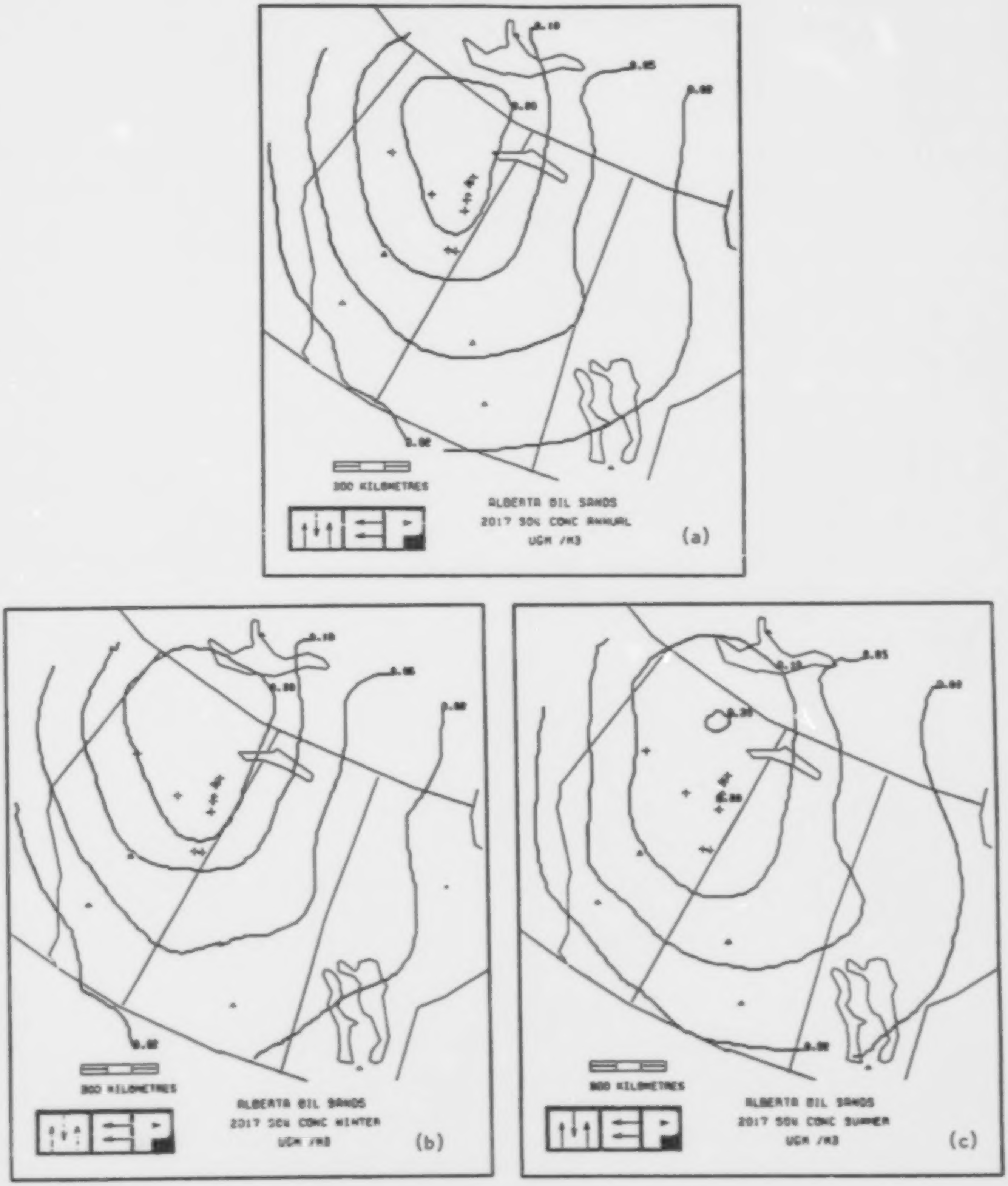
0.10
0.05
0.02
0.20
0.02
300 KILOMETRES
MEP
ALBERTA OIL SANDS
2017 SO4 CONC ANNUAL
UGM /M3
(a)
0.10
0.05
0.02
0.20
0.02
300 KILOMETRES
MEP
ALBERTA OIL SANDS
2017 SO4 CONC WINTER
UGM /M3
(b)
0.10
0.05
0.02
0.30
0.20
0.02
300 KILOMETRES
MEP
ALBERTA OIL SANDS
2017 SO4 CONC SUMMER
UGM /M3
(c)

Figure 8. Predicted 2017 SO_4 concentrations ($\mu g/m^3$).

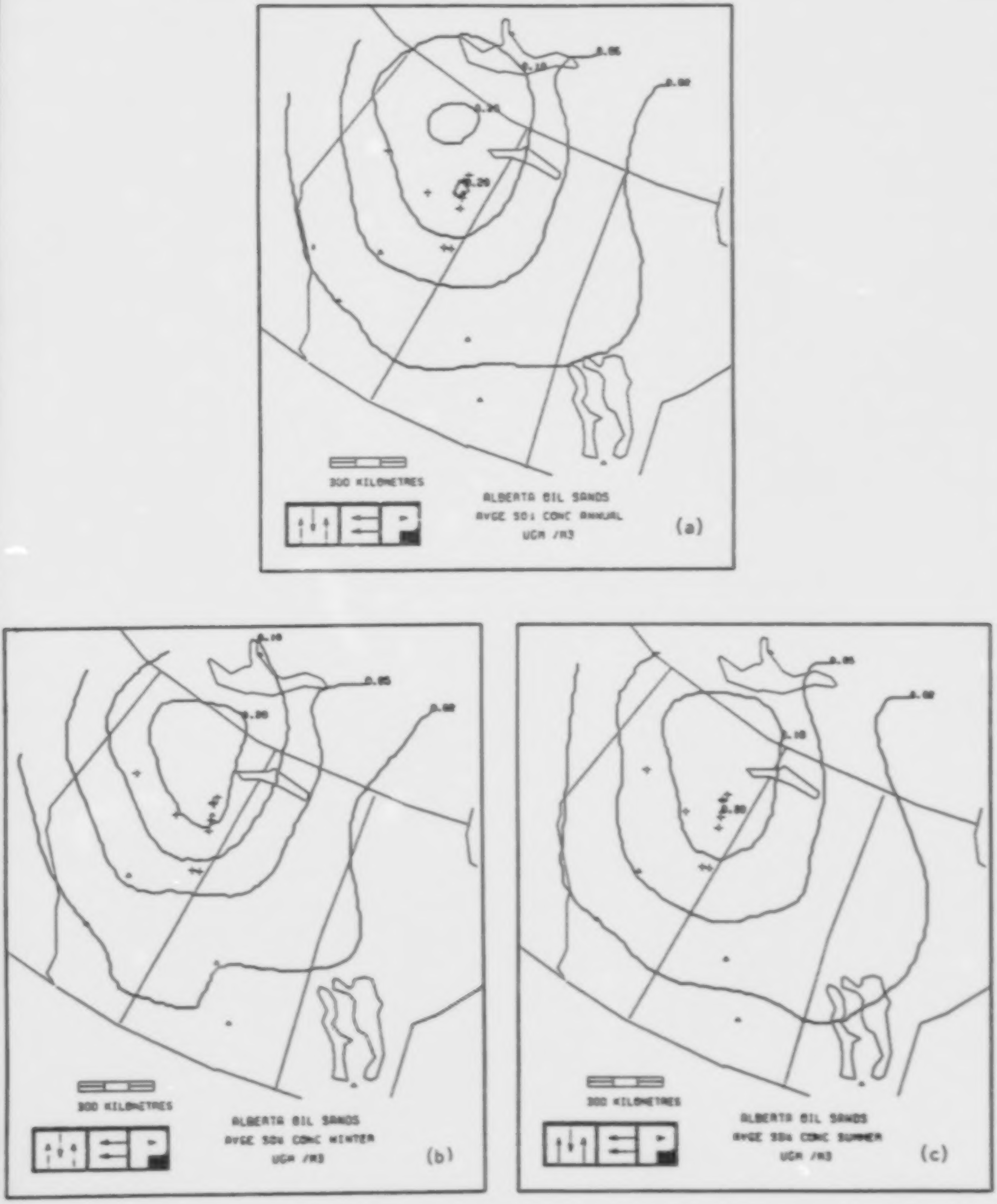
0.05
0.10
0.02
0.20
0.20
300 KILOMETRES
ALBERTA OIL SANDS
AVGE SO4 CONC ANNUAL
UGM /M3
(a)
0.10
0.05
0.20
0.02
0.40
300 KILOMETRES
ALBERTA OIL SANDS
AVGE SO4 CONC WINTER
UGM /M3
(b)
0.05
0.02
0.10
0.20
300 KILOMETRES
ALBERTA OIL SANDS
AVGE SO4 CONC SUMMER
UGM /M3
(c)

Figure 9. Predicted average SO_4 concentrations ($\mu g/m^3$).

The full maps of sulphate concentrations are displayed in Figures 7a to 7c for the 1980 emissions, and Figures 8a to 8c for the 2017 and long-term average emissions respectively. The peak sulphate concentration is just over 0.2 g/m^3 annual average, dropping to less than 0.1 g/m^3 at 300 km. The winter concentrations are 25% higher than the summer, but the fields of concentration all show the same flat gradients with distance.

The sulphate concentrations in 2017 show a 50% increase over 1980, with a maximum of 0.31 g/m^3 annual average. This increase is much greater than that for SO_2 due to the slower drop-off of concentration with distance from the sources, allowing for a greater superposition of the multiple sources.

The total deposition of sulphur (wet plus dry) is shown in Figures 10a to 10c, 11a to 11c, and 12a to 12c. The long-term mean loading of sulphur has a peak value of 4.0 kg/ha per year in the region of Fort McMurray, the wet component contributing 40% of this value. This drops to 1 kg/ha within 300 km of Fort McMurray.

The long-term loading of nitrogen (wet plus dry) is shown in Figure 13, and shows a peak rate of 0.44 kg/ha per year as nitrogen, this being approximately 10% of the sulphur loading.

The pattern of sulphur and nitrogen loading has been further summarized in Table 6, which represents the mean loading over all receptors within a given distance range from Fort McMurray for the 1980 emissions. Thus the mean loading of sulphur in the range of 0 to 100 km is 3.66 kg/ha, with wet deposition accounting for 40% of the deposition. In the distance range of 300 to 500 km, the average total loading is only 0.24 kg/ha, with wet loading accounting for 50%.

The average loadings over the indicated ranges can also be used to determine the total deposition of sulphur and nitrogen as a function of emissions. It is found that approximately 25% of the emissions are deposited within 200 km of the sources, 40% of the sulphur emissions are deposited within the first 500 km. For nitrogen, the corresponding fractions are 21% and 32% of annual emissions.

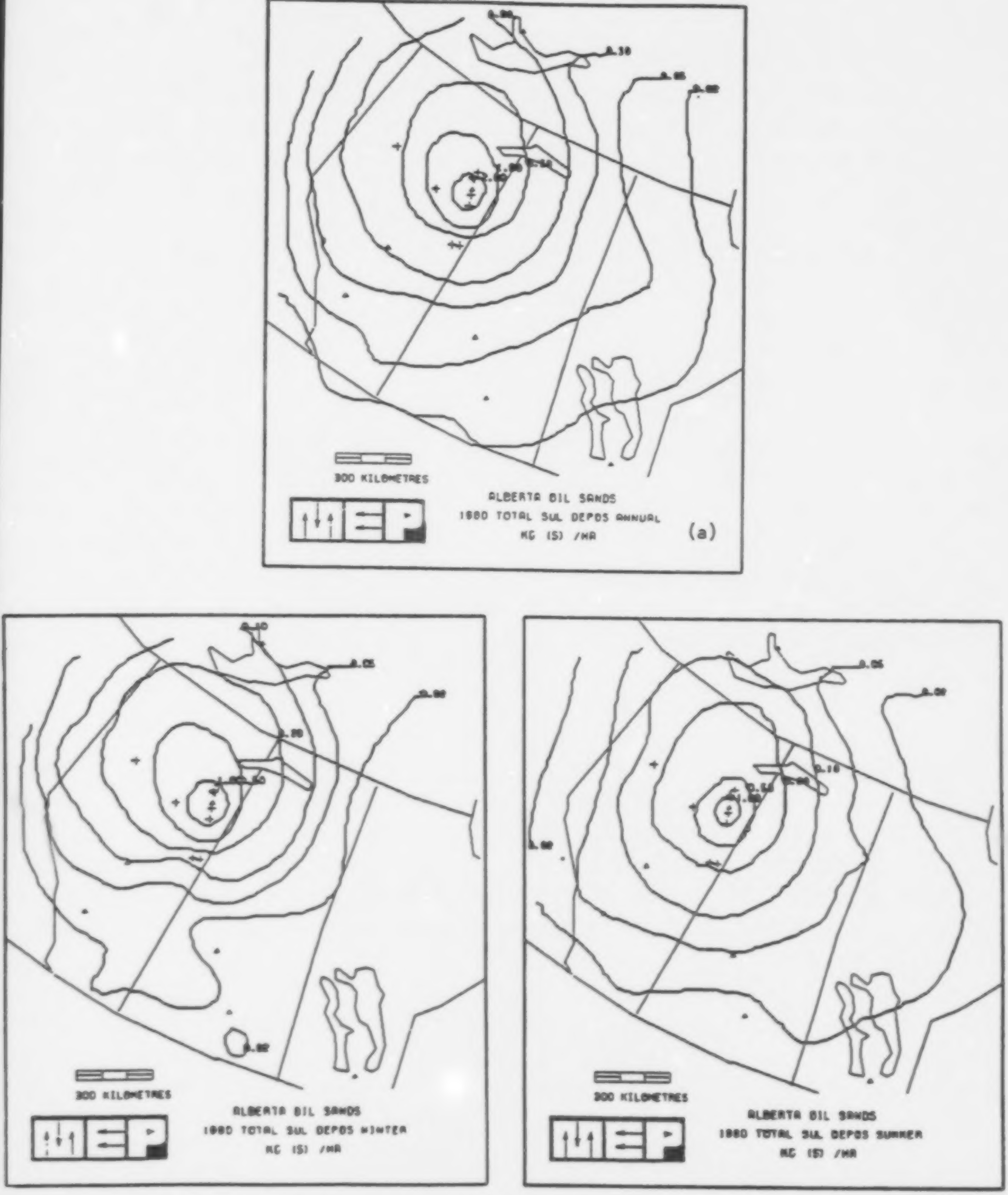
0.80
0.10
0.05
0.02
300 KILOMETRES
ALBERTA OIL SANDS
1980 TOTAL SUL DEPOS ANNUAL
KG (S) /HA
(a)
0.10
0.05
0.02
0.80
300 KILOMETRES
ALBERTA OIL SANDS
1980 TOTAL SUL DEPOS WINTER
KG (S) /HA
0.05
0.02
0.10
300 KILOMETRES
ALBERTA OIL SANDS
1980 TOTAL SUL DEPOS SUMMER
KG (S) /HA

Figure 10. Predicted 1980 total sulphur deposition (kg/ha).

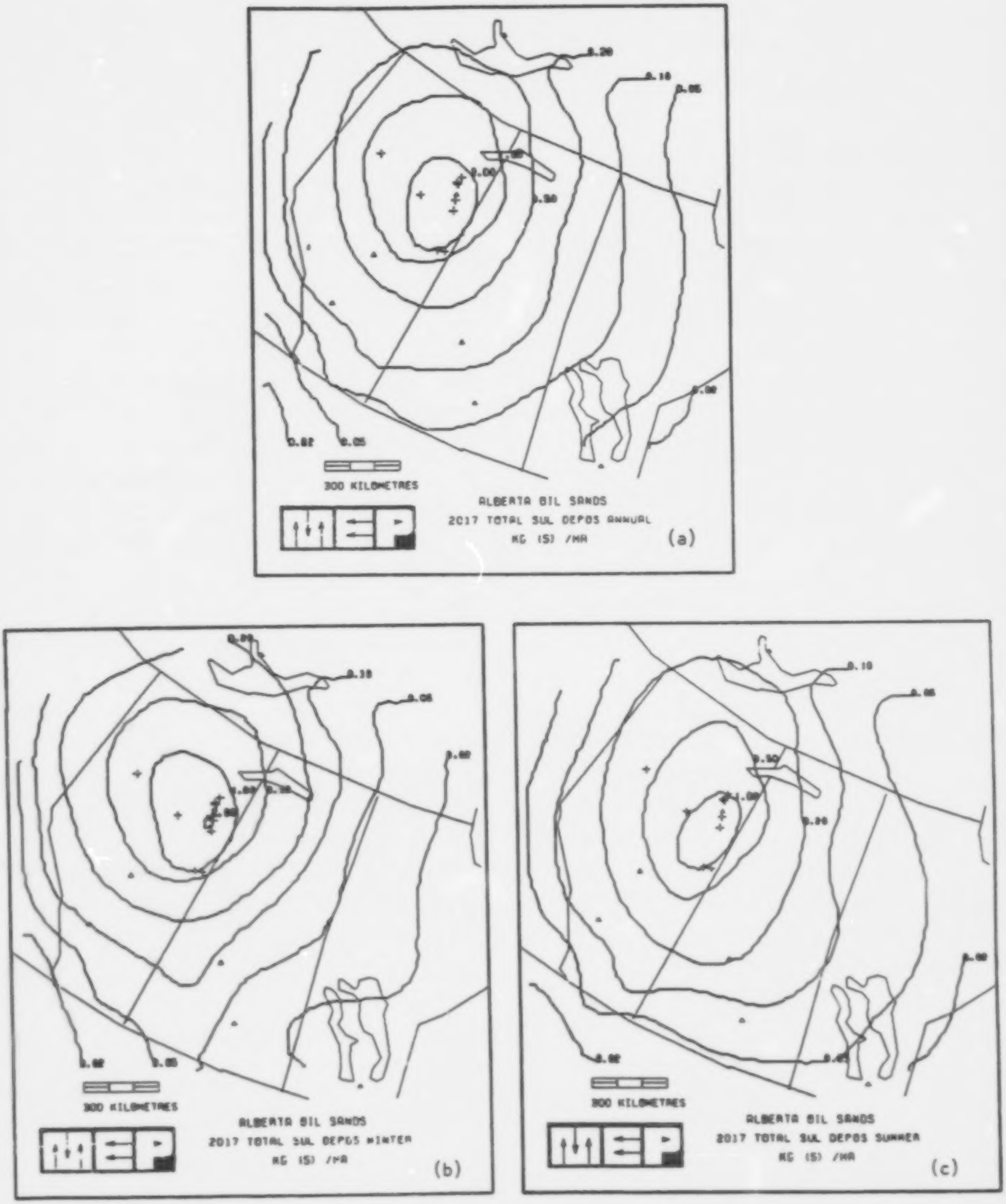
0.20
0.10
0.05
0.50
0.02
0.05
300 KILOMETRES
ALBERTA OIL SANDS
2017 TOTAL SUL DEPOS ANNUAL
KG (S) /HA
(a)
0.10
0.05
0.02
0.02
0.05
300 KILOMETRES
ALBERTA OIL SANDS
2017 TOTAL SUL DEPOS WINTER
KG (S) /HA
(b)
0.10
0.05
0.50
1.00
0.20
0.02
0.02
0.05
300 KILOMETRES
ALBERTA OIL SANDS
2017 TOTAL SUL DEPOS SUMMER
KG (S) /HA
(c)

Figure 11. Predicted 2017 total sulphur deposition (kg/ha).

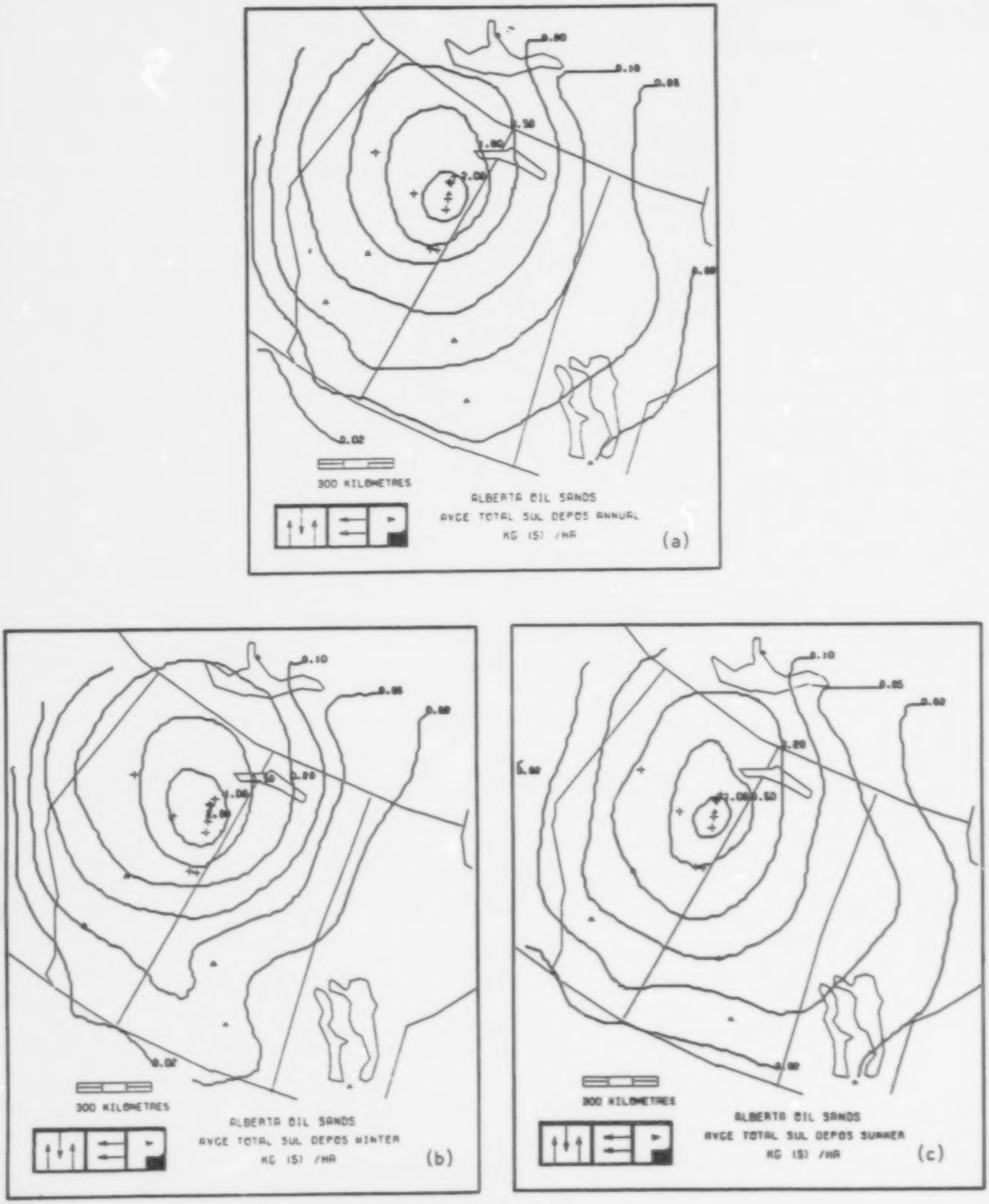
0.20
0.10
0.05
0.50
1.00
2.00
0.02
300 KILOMETRES
ALBERTA OIL SANDS
AVGE TOTAL SUL DEPOS ANNUAL
KG (S) /HA
(a)
0.10
0.05
0.02
0.50
1.00
2.00
0.20
300 KILOMETRES
ALBERTA OIL SANDS
AVGE TOTAL SUL DEPOS WINTER
KG (S) /HA
(b)
0.10
0.05
0.02
0.20
1.00
0.50
300 KILOMETRES
ALBERTA OIL SANDS
AVGE TOTAL SUL DEPOS SUMMER
KG (S) /HA
(c)

Figure 12. Predicted Average Total Sulphur Deposition (kg/ha).

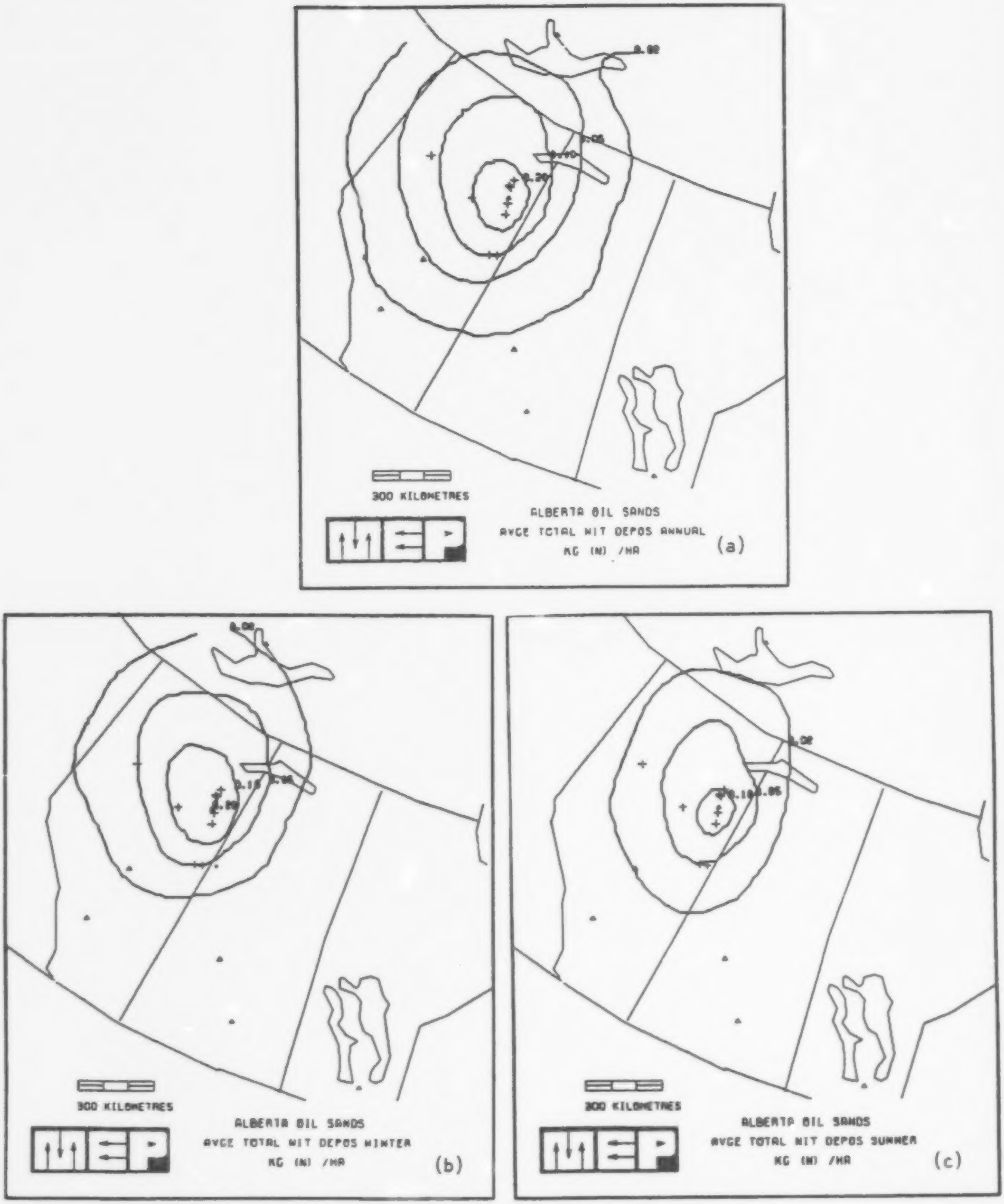
0.02
0.05
0.10
0.20
0.40
300 KILOMETRES
ALBERTA OIL SANDS
AVGE TOTAL NIT DEPOS ANNUAL
KG (N) /HA
(a)
0.02
0.05
0.10
0.20
300 KILOMETRES
ALBERTA OIL SANDS
AVGE TOTAL NIT DEPOS WINTER
KG (N) /HA
(b)
0.02
0.10
0.05
300 KILOMETRES
ALBERTA OIL SANDS
AVGE TOTAL NIT DEPOS SUMMER
KG (N) /HA
(c)

Figure 13. Predicted average total nitrogen deposition (kg/ha).

Table 6. Mean loading for 1980 emissions as a function of distance from Fort McMurray.

Distance Range	Sulphur Deposition (kg S/ha)			Nitrogen Deposition (kg N/ha)		
	Wet	Dry	Total	Wet	Dry	Total
0 - 100	1.43	2.23	3.66	0.12	0.21	0.32
100 - 200	0.42	0.53	0.95	0.03	0.05	0.08
200 - 300	0.27	0.32	0.59	0.02	0.03	0.05
300 - 500	0.12	0.12	0.24	0.01	0.01	0.02
500 - 700	0.06	0.08	0.14	0.01	0.01	0.01

6. CONCLUSIONS

The results discussed in Section 5 indicate that the projected increase in SO_2 and NO_x emissions from the development of Oil Extraction Plants to the year 2017 will result in an increase in the amount and distribution of loadings of sulphur and nitrogen in Alberta and surrounding regions. The predicted increase is, in general, less than the two-fold increase in emissions over the period from the present (1980) to 2017. This results from the more distributed nature of emissions in the later periods of the development.

Although this study does not address the issue of the impact on the environment of the projected loadings, a comparison of the long-term average loadings predicted with the criterion for loading in ecologically sensitive regions, being contemplated by the Federal Department of Environment, of 20 kg SO_4/ha shows that the projected loadings in the Northern Saskatchewan sensitive regions would amount to approximately 2% of the recommended criterion level.

There are a number of sources of uncertainty in the projections, including: the projected emissions configuration; the selection of transformation and removal parameters for the dispersion modelling; the representativeness of the long-term meteorology; and the model uncertainty.

The emissions inventory projections are thought to be an over-estimate, presenting a "worst case" situation by the year 2017. Thus, this source of error will tend to over-predict the potential loadings to the environment.

The choice of removal and transformation parameters, since it is based primarily on data for other regions, is more problematic. Sensitivity tests of the model to choice of parameters, when evaluated over a complete year, show that realistic variation of parameters generates less than a two-fold variation in loadings predictions. Coupled with the year to year variation in meteorology and its effect on long-term averages, it is anticipated that a factor of two potential error in the projections would be realistic. This type of factor should be considered when assessing absolute predictions generated by the model.

7. ACKNOWLEDGEMENT

The work reported in the paper was sponsored by the Oil Sands Environmental Study Group, and their support is gratefully acknowledged.

8. REFERENCES

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Weisman, B. 1981. Application of trajectory model to regional characterization. In 12th International Technical Meeting on Air Pollution Modelling and its Application. Palo Alto, California.

MODELLING LRTAP IN WESTERN CANADA

P. KOCIUBA[1]

ABSTRACT

Several models have been developed in Canada and the United States to assess the rate of deposition at the earth's surface of atmospheric pollutants, some of which may have travelled great distances from industrial source areas. Although these models do have restrictions on their usefulness, they are an important tool and possibly the only guide available to evaluate the environmental impact of atmospheric pollutants at great distances from the source.

To date, virtually all applications of LRTAP models have been to eastern North America, the zone of maximum acidity, and to western Europe. It is the intent of this study to estimate the probable acid loading from industrial sources by applying the AES-LRTAP model to locations in western Canada.

The AES-LRTAP model consists of two major modules, namely a Lagrangian three-dimensional trajectory model and a box concentration/deposition model.

The three-dimensional trajectory model uses objectively analyzed wind fields and computes vertical motions by the "omega" equation at 850, 700, and 500 mb as well as mountain and friction-induced vertical motions at the 1 000 mb level. Input wind fields are available every six hours and interpolation routines, bi-cubic in the vertical and bi-linear in the horizontal, are used to obtain winds at intermediate positions in time and space. The computations are performed on the standard Canadian Meteorological Centre grid of 381 km at 60°N. Trajectory segment endpoints are determined each time-step by assuming constant acceleration and using an iterative scheme. The motion of air parcels can be followed backward (receptor mode) or forward (source mode) from anywhere in North America.

For the current study, 18 stations were selected by AES (Central, Western and Pacific regions) for back trajectories and four stations for forward trajectories. All trajectories were computed at the 850-mb level except for Cree Lake at 925 mb, Vancouver at 925 mb, and Hat Creek at 700 mb. Trajectories are calculated for each site four times (00, 06, 12, 18 GMT) each day for a period of four days based on six-hour time steps within the four-day period (1978 data year).

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An analysis of the trajectory endpoints was undertaken to determine the origin or destination of air parcels from the receptor or source in terms of direction and distance. In addition, the air parcel elevation as a function of direction and horizontal distance was analyzed. The results of this analysis indicated that a preliminary concentration/deposition model output run was warranted.

The concentration/depositon box model utilizes the results of the trajectory model. Trajectory paths are computed across grid cells of pollutant emission, monthly mixing height and daily precipitation amount. Uniform vertical mixing is assumed to occur instantaneously up to the mixing height. Pollutant removal is linearly parameterized by wet and dry deposition and chemical transformation (Olson, et al. 1979). Pollutant input to each box is provided from an annual North American SO_2 emissions inventory on a 127-km grid (Voldner and Shah, 1980).

The SO_2 to SO_4^{--} chemical transformation rate is assumed to be constant. Dry deposition is parameterized in terms of deposition velocities; wet deposition, by scavenging ratios and by a gridded daily array of precipitation amount.

The model calculates not only SO_2 and SO_4^{--} concentrations but also dry and wet deposition fluxes. These quantities are computed up to four times per day of the month to produce daily and monthly averages and totals for each station.

A preliminary model run will be undertaken on trajectory data for July 1978 for all receptor sites. The computed SO_4^{--} concentrations will be compared with measured values at precipitation sampling stations. The results of such an analysis will indicate whether a complete concentration/deposition model output will be produced for all computed 1978 trajectories.

If this feasibility study yields positive results, future plans will be to prepare contoured maps of concentrations/deposition patterns over sensitive areas of western Canada, not only for the analysis years but with emissions estimates in the future.

1. INTRODUCTION

Several models have been developed in Canada and the United States to assess the rate of deposition at the earth's surface of atmospheric pollutants, some of which may have travelled great distances from industrial source areas. Although these models do have restrictions on their usefulness, they are an important tool and possibly the only guide available to evaluate the environmental impact of atmospheric pollutants at great distances from the source.

To date, virtually all applications of Long Range Transport of Atmospheric Pollutants (LRTAP) models have been to eastern North America, the zone of maximum acid deposition, and to western Europe. It is the intent of this study to apply the Atmospheric Environment Service (AES) LRTAP model to locations in western Canada and assess its ability to estimate probable sulphate deposition resulting from industrial emissions in the western part of North America. For this purpose, meteorological emissions and precipitation chemistry data for the calendar year 1978 have been used.

2. MODEL DESCRIPTION

The AES LRTAP model consists of two major modules; a Lagrangian three-dimensional trajectory model, and a box concentration/deposition model.

The three-dimensional trajectory model uses objectively analyzed wind fields and computes vertical motions by the "omega" equation at 850, 700, and 500 mb as well as mountain and friction-induced vertical motions at the 1 000 mb level. Input wind fields are available every six hours and interpolation routines, bi-cubic in the vertical and bi-linear in the horizontal, are used to obtain winds at intermediate positions in time and space. The computations are performed on the standard Canadian Meteorological Centre grid of 381 km at 60^{o}N. Trajectory segment endpoints are determined each time-step by assuming constant acceleration and using an iterative scheme. The motion of air parcels can be followed backwards (receptor mode) or forwards (source mode) from anywhere in North America.

For the current study, 16 stations were selected for back trajectories and four stations for forward trajectories. The locations of these stations are shown in Figure 1. All trajectories were computed at the 850 mb level except for Cree Lake and Vancouver at 925 mb and 850 mb, and Hat Creek at 700 mb only. Trajectories were calculated for each site four times (00,600,1800 GMT) each day for a duration of four days using six-hour time steps.

An analysis of the trajectory endpoints was undertaken to determine the origin or destination of air parcels from the receptor or source in terms of a 2.5° latitude by 5° longitude square. In addition, the elevation of air parcels was also analyzed using the above method. The analysis of air parcel elevation yielded some interesting results. As expected, trajectory elevation increased as the air parcels moved over higher terrain but, on an annual average, show a decrease in elevation once over the ocean. During this analysis, instances were found where the air trajectory elevation was at sea level over the ocean. It was determined that the model derived trajectories from both sources and receptors were reasonable in terms of western Canada synoptic patterns and did not appear to be over-influenced by the topography in the western part of the area.

The concentration/deposition box model utilizes the results of the trajectory model. Trajectory paths are computed across grid cells of pollutant emission, monthly mixing height and daily precipitation amount. Uniform vertical mixing is assumed to occur instantaneously up to the mixing height. Pollutant removal is linearly parameterized by wet and dry deposition and chemical transformation (Olson et al. 1979). Pollutant input to each box is provided from an annual North American SO_2 emissions inventory on a 127 km grid (Voldner et al. 1980) as shown in Figure 2.

The SO_2 to SO_4 chemical transformation rate is assumed to be constant. Dry deposition is parameterized in terms of deposition velocities; wet deposition, by scavenging ratios and by a gridded daily array of precipitation amount.

The model calculates not only SO_2 and $SO_4^=$ concentrations but also dry and wet deposition fluxes. These quantities are computed up to four times per day each day of the month to produce daily and monthly averages and totals for each station.

For the purpose of this study, only wet deposition calculations were made to check against results from the CANSAP network.

3. DISCUSSION

3.1 TRAJECTORY ANALYSIS FOR SOURCES

3.1.1 Fort McMurray, Alberta (Figures 3 to 6)

Annual trajectory end-point frequencies are illustrated in Figures 3 to 6 for 24-hr, 48-hr, 72-hr, and 96-hr respectively. The values plotted and contoured indicate the frequency of end-point trajectories which crossed the 2.5° latitude by 5° longitude square, scaled by the area subtended on the earth's surface.

At the of the 24-hr period, the maximum frequency of end-points is aligned in a northwest-southeast direction east of Fort McMurray. In 48 hours, the trajectory maximum has moved eastward but the northwest-southeast orientation is maintained. Some end-points have spread well into the Arctic and eastern Canada.

In 72 hours, further spread is evident with maximum frequency patterns identifiable in the Northwest Territories, Saskatchewan and Manitoba. The 96-hr pattern is similar.

3.1.2 Hat Creek, British Columbia (Figures 7 to 10)

For this site, the model was run at 700 mb to reduce topographic effects. Trajectory end-points follow the general west-east circulation pattern but for time periods greater than 24 hours, there are significant north and south components.

3.1.3 Thompson, Manitoba (Figures 11 to 14)

The expected pattern of end-point distribution resulting from a westerly circulation is evident at this site (850 mb). There appears to be a significant frequency of end-points to the west of the source point for each time interval. Whether this results from synoptic weather patterns unique to the 1978 data set or whether it is a normal feature of this area will have to be examined further. This westward motion may also be the result of upslope easterly circulation at certain times of the year.

3.1.4 Dawson Creek, British Columbia (Figures 15 to 18)

The annual trajectory end-point frequencies (850 mb) exhibit a northwest-southeast orientation similar to the results for Fort McMurray.

3.2 TRAJECTORY ANALYSIS FOR RECEPTORS

3.2.1 Cree Lake, Saskatchewan (Figures 19 to 22)

Since back trajectories calculated for several sites show similar features, only those for Cree Lake are included here. Highest points frequencies for all four time periods are northwest of Cree Lake. There is little difference between the 48-hr and 96-hr start-point distributions at the 850 mb level except that the degree of spread becomes pronounced at 96-hr.

3.2.2 Comparison of 850 mb and 925 mb Trajectories (Figures 23 and 24)

Figures 23 and 24 show the start-point frequencies for Cree Lake at the 925 mb level for comparison. For the 48-hr period, there is a virtual overlap of maxima with a tendency for the 850 mb level trajectories to be further upstream resulting from the stronger flow.

By 72 hours, a spread is noticeable with a maximum still in the Mackenzie Valley but secondary maxima in the Pacific, Hudson Bay, and the Arctic Islands. The difference between the 850 mb and 925 mb levels however, is not great.

3.3 CONCENTRATION-DEPOSITION

Estimating concentrations and deposition involved the use of a box model with trajectories, emissions and precipitation as the primary input. For the initial part of the study only data from July 1978 were used. The emissions data used are organized on a grid of 127 km by 127 km.

Several features became apparent at this stage:

1. Sulphur emissions are low compared with eastern North America with a small number of identifiable sources areas: western foothills of Alberta (gas); northeastern B.C. (gas); Fort McMurray (oil sands); Flin Flon and Thompson (mining and smelting);
2. Emissions in western U.S.A. are reported as state totals only and subjectively assigned to grid points;
3. Estimated possible errors in emissions may vary from 20-50%.

3.3.1 Deposition Model Results

The model exhibited the same tencies as in eastern Canada applications to under-predict wet sulphate deposition at receptors remote from major sources. In applying the model to Cree Lake for July 1978, a value for wet sulphate deposition of 0.09 mg/L is derived. The measured wet sulphate deposition in that period was 0.6 mg/L. The difference may be attributed to "natural emissions or background". This assumption takes on some validity when it is noted that if the same value, being the lowest measured value and thus assumed to be a representative background value, is added to calculated wet sulphate deposition for each of the receptor sites, the model results become much closer to those measured by the CANSAP stations. Figure 25 and 26 show a comparison of calculated and measured wet sulphate deposition at several western locations.

Two factors are evident from Figure 25:

1. The sulphate component resulting from long-range transport of industrial pollutants is small; and
2. Measured sulphate in precipitation samples is relatively small at most sites.

Some sites such as Coronation, Suffield and Fort McMurray indicate relatively higher levels of $SO_4^=$. The corresponding high concentrations of calcium, potassium, and magnesium indicate the presence of wind blown dust. These data must be evaluated further before further judgments can be made.

4. CONCLUSIONS

This project has demonstrated that the AES LRTAP model can be applied and yield valid results within the limits of data availability in western Canada.

5. RECOMMENDATIONS

1. Complete analysis of trajectories for 1979 and 1980 to refine and extend confidence in results of 1978 estimates.
2. Extend analysis of trajectories to other significant sources in Western Canada for the years 1978 to 1980.
3. Investigate background SO_4 levels in western Canada and conduct quality control study of CANSAP data in western Canada.
4. Investigate high SO_4 levels at specific sites (Coronation, Suffield).
5. Modify and update emissions inventories and run concentration/deposition model for other seasons and the full year of 1978.
6. Produce projected emissions to future years and run model to map deposition patterns.

6. REFERENCES CITED

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United States-Canada. July 1981. Memorandum of Intent on Transboundary Air Pollution, Phase 2 Interim Report, Working Group 2.

Voldner, E.C., et al. 1980. A preliminary Canadian emissions inventory for sulphur and nitrogen oxides. Atmospheric Environment. 14:419-428.

Walmsley, J.L., J. Mailhot and R.F. Hopkinson. 1981. Sensitivity tests with a trajectory model. AORB 81-027-L. Atmospheric Environment Service. pp. 49.

7. APPENDIX: Figures 1 to 26

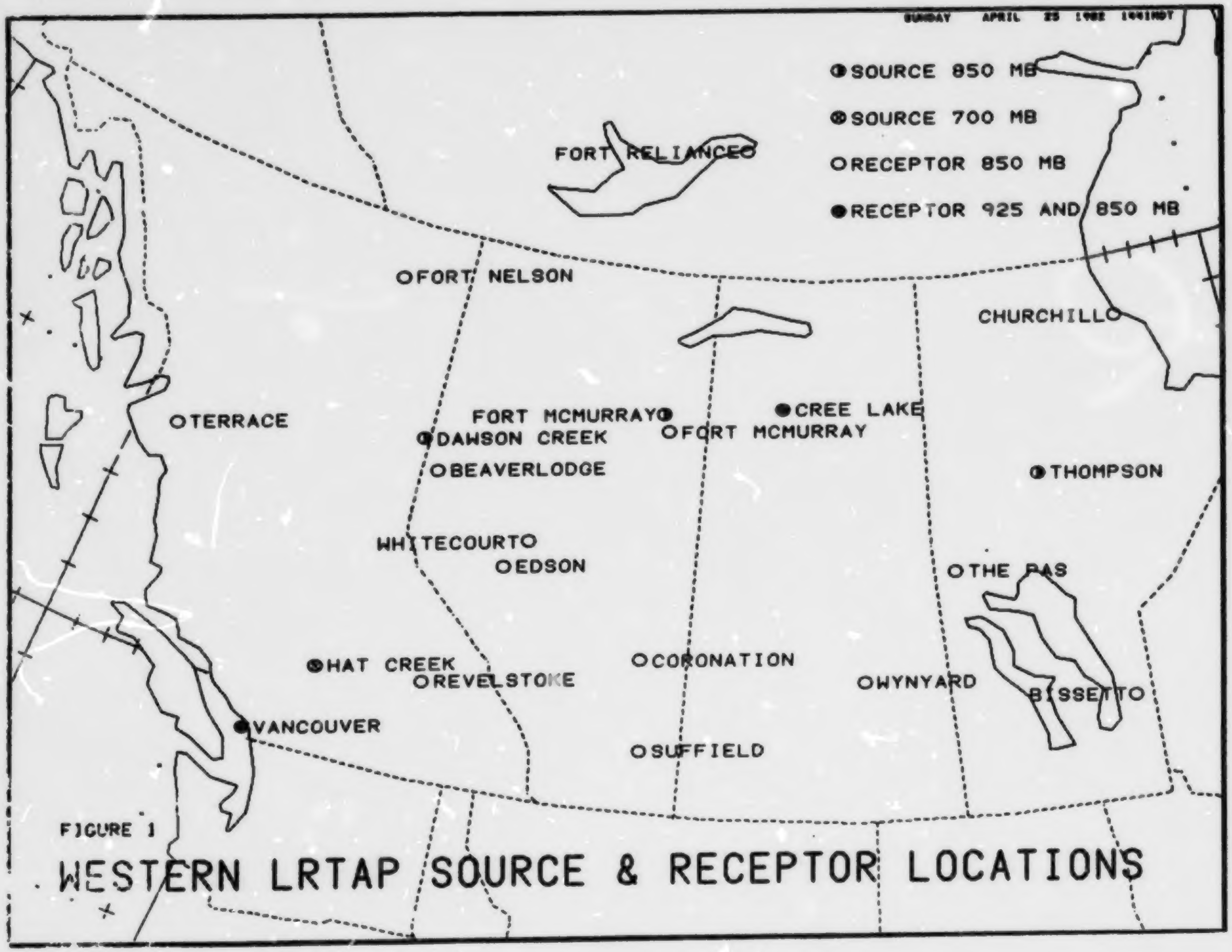

SUNDAY APRIL 25 1982 1441MDT
◐SOURCE 850 MB
⊗SOURCE 700 MB
○RECEPTOR 850 MB
●RECEPTOR 925 AND 850 MB
FORT RELIANCE○
○FORT NELSON
CHURCHILL○
FORT MCMURRAY◐
●CREE LAKE
○FORT MCMURRAY
○TERRACE
⊗DAWSON CREEK
○BEAVERLODGE
◐THOMPSON
WHITECOURT○
○EDSON
○THE PAS
⊗HAT CREEK
○REVELSTOKE
○CORONATION
○WYNYARD
BISSETT○
●VANCOUVER
○SUFFIELD

FIGURE 1

WESTERN LRTAP SOURCE & RECEPTOR LOCATIONS

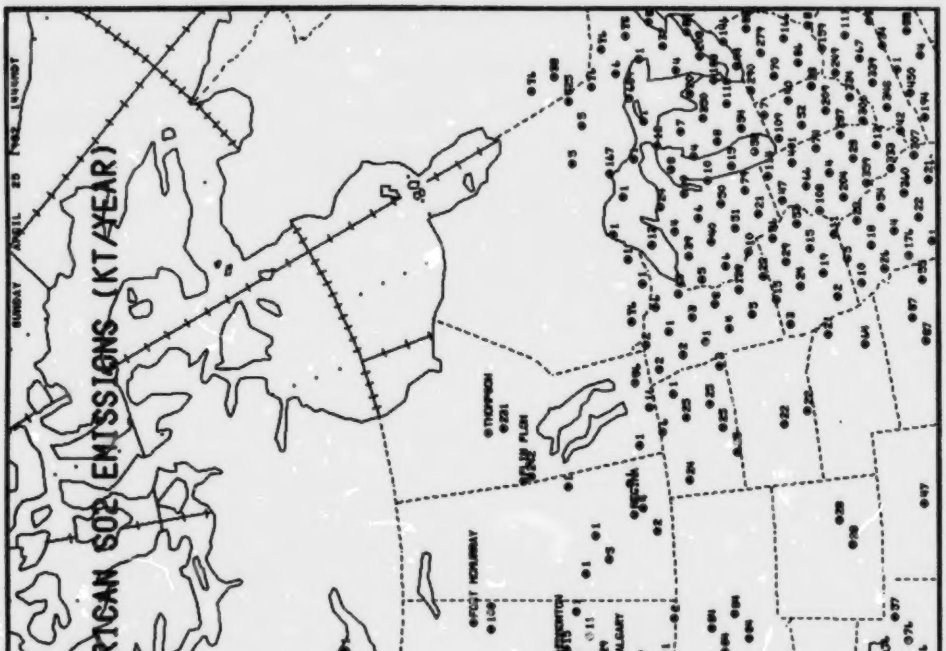


FIGURE 2 1978 TOTAL NORTH AMERICAN SO2 EMISSIONS (KT/YEAR)

140
50
80
THOMPSON
FORT MCMURRAY
EDMONTON
CALGARY

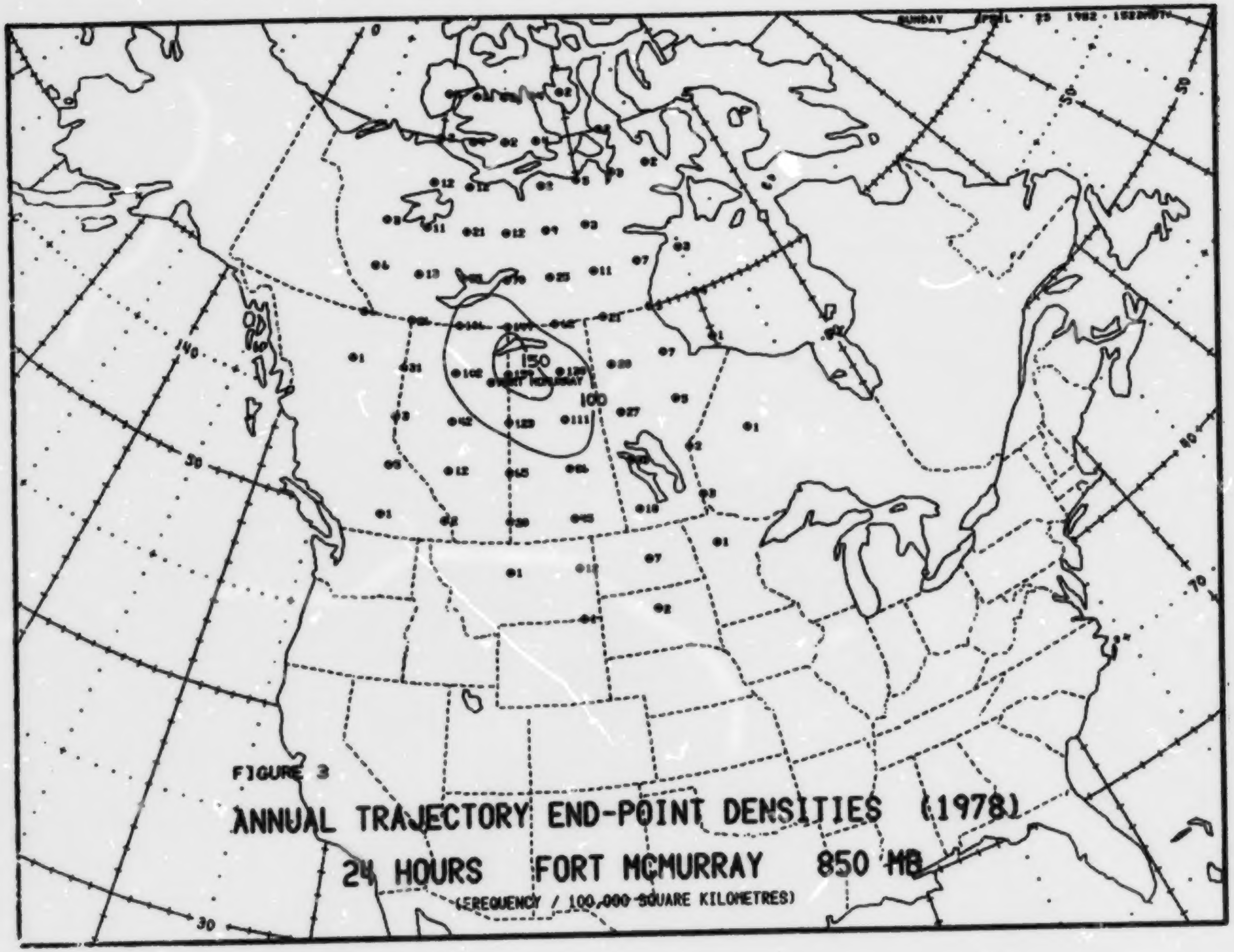
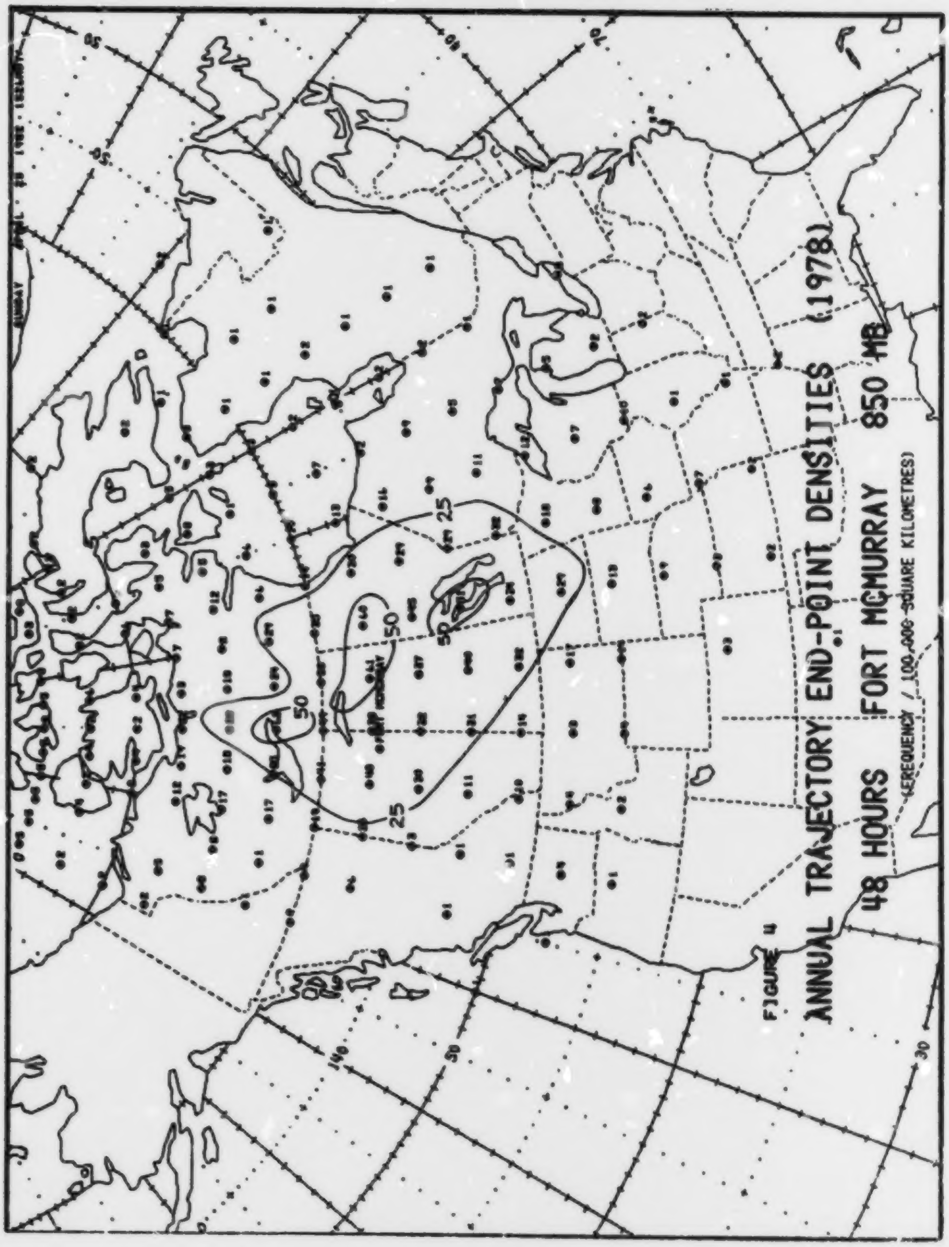

SUNDAY APRIL 25 1982 1523MDT
150
100
FORT MCMURRAY
0
140
50
30
50
50
60
70
80

FIGURE 3

ANNUAL TRAJECTORY END-POINT DENSITIES (1978)

24 HOURS FORT MCMURRAY 850 MB

(FREQUENCY / 100,000 SQUARE KILOMETRES)



25
50
50
25
FORT MCMURRAY
30
30

FIGURE 4

ANNUAL TRAJECTORY END-POINT DENSITIES (1978)

48 HOURS FORT MCMURRAY 850 MB

(FREQUENCY / 100,000 SQUARE KILOMETRES)

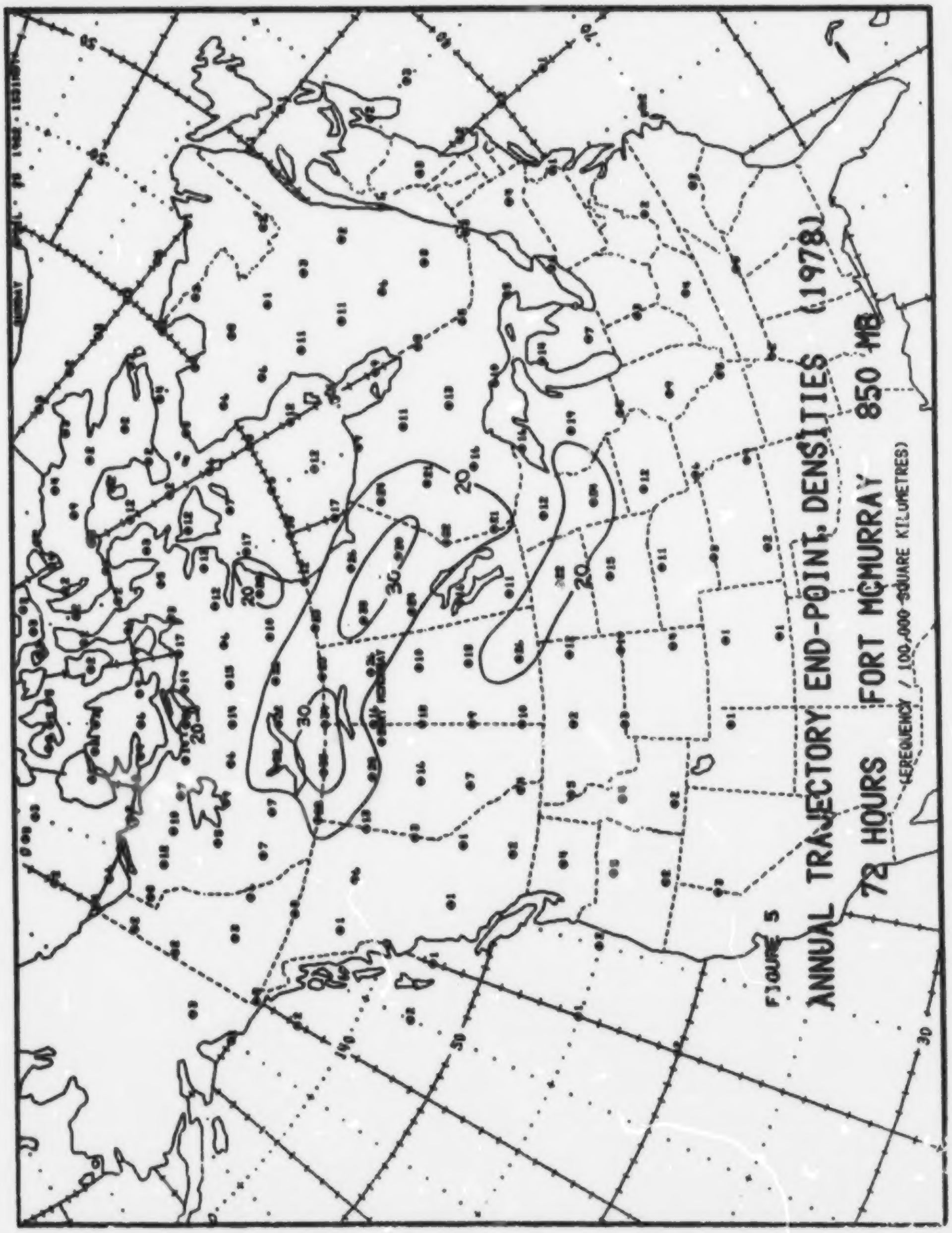


FIGURE 5

ANNUAL TRAJECTORY END-POINT DENSITIES (1978)

72 HOURS FORT MCMURRAY 850 MB

(FREQUENCY / 100,000 SQUARE KILOMETRES)

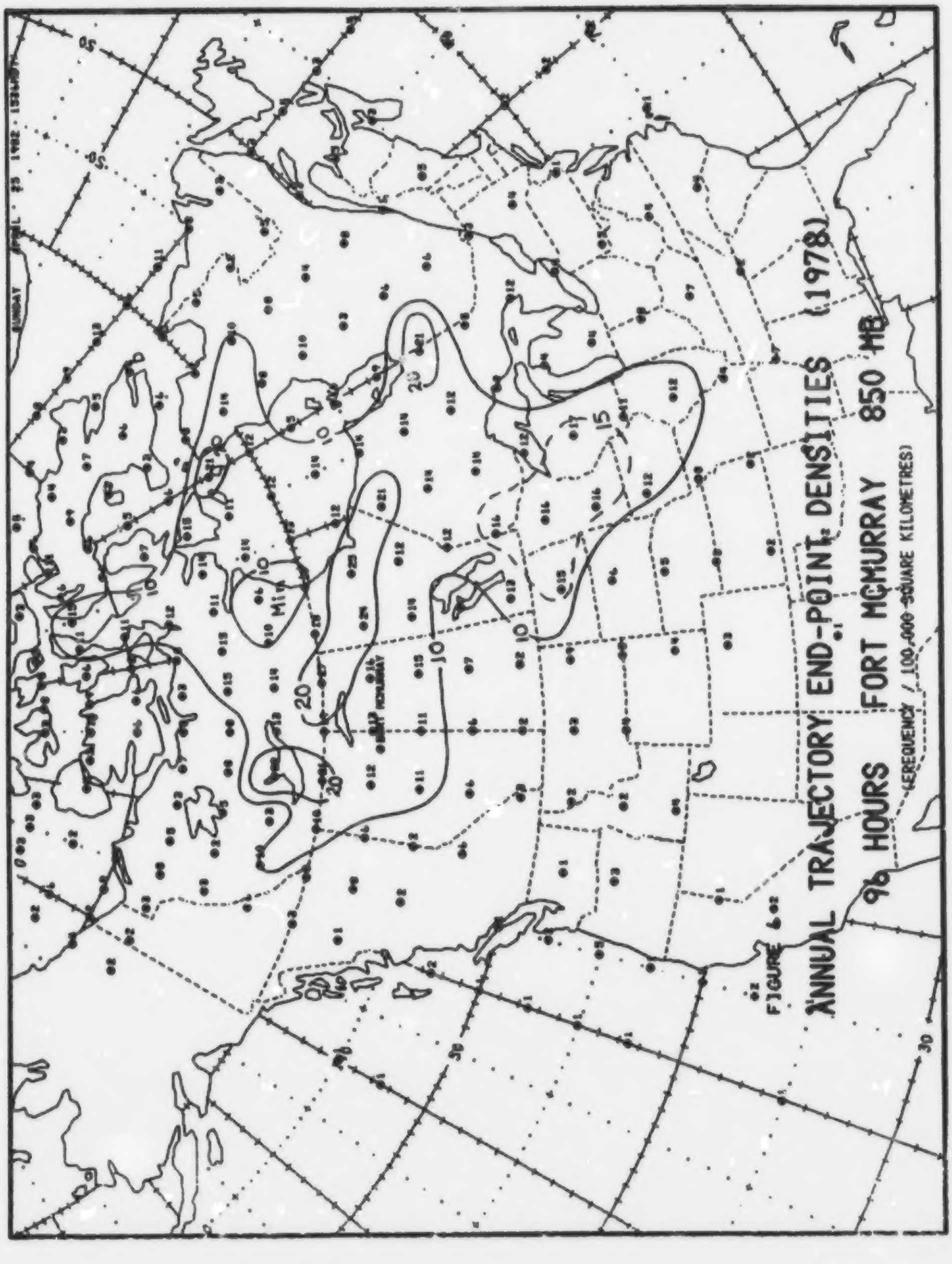


FIGURE 6

ANNUAL TRAJECTORY END-POINT DENSITIES (1978)

96 HOURS FORT MCMURRAY 850 MB

(FREQUENCY / 100,000 SQUARE KILOMETRES)

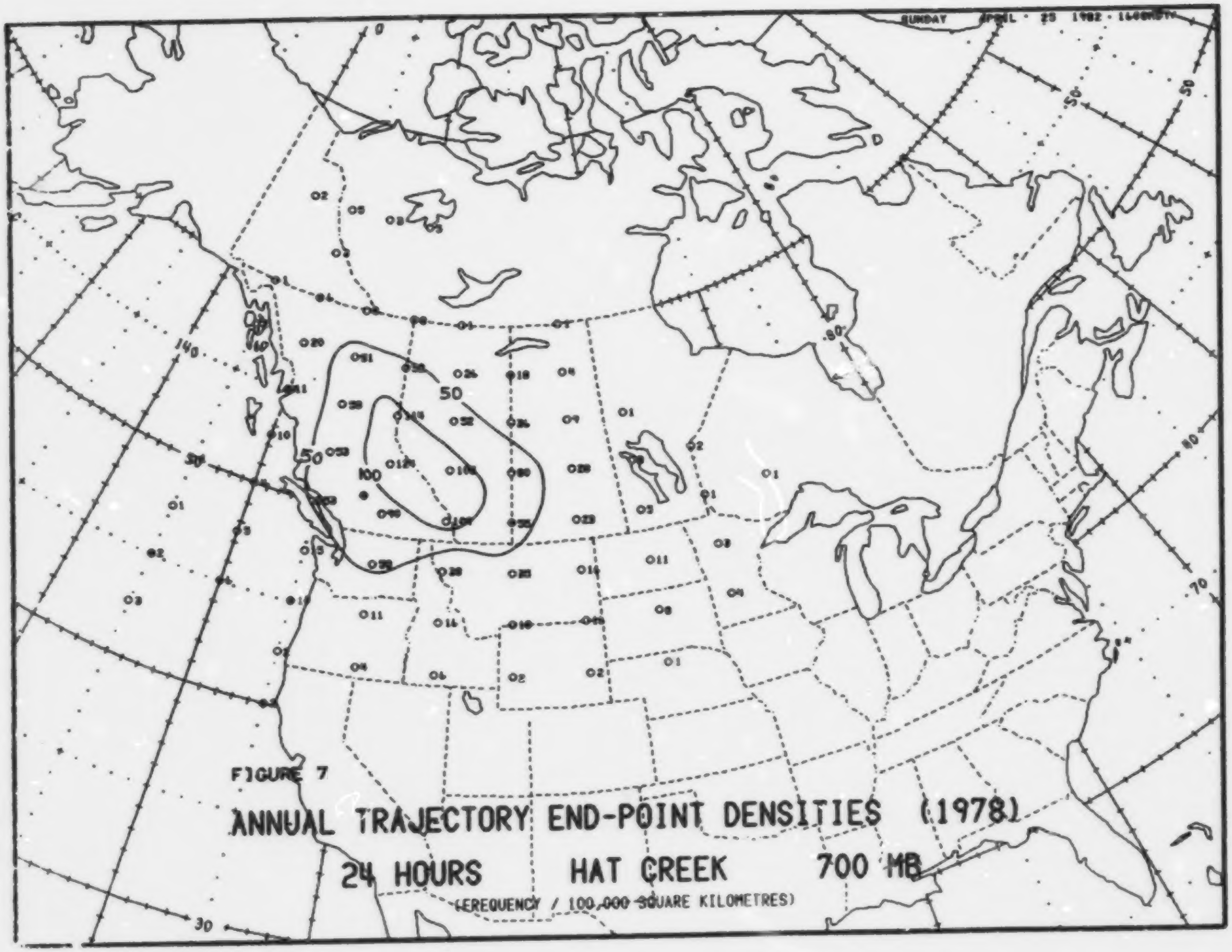

50
100
50
140
30
50
80
70
30

FIGURE 7

ANNUAL TRAJECTORY END-POINT DENSITIES (1978)

24 HOURS HAT CREEK 700 MB

(FREQUENCY / 100,000 SQUARE KILOMETRES)

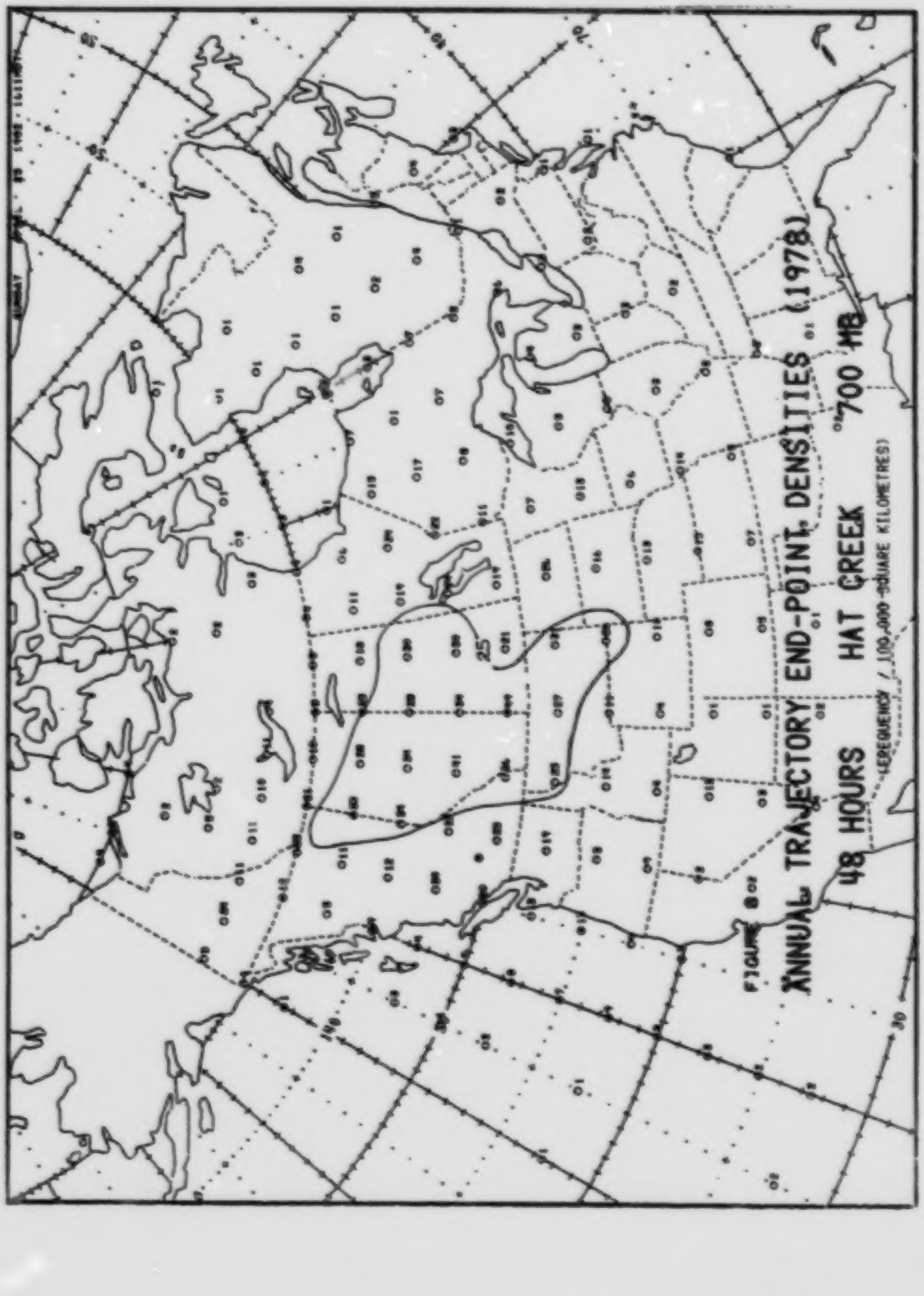
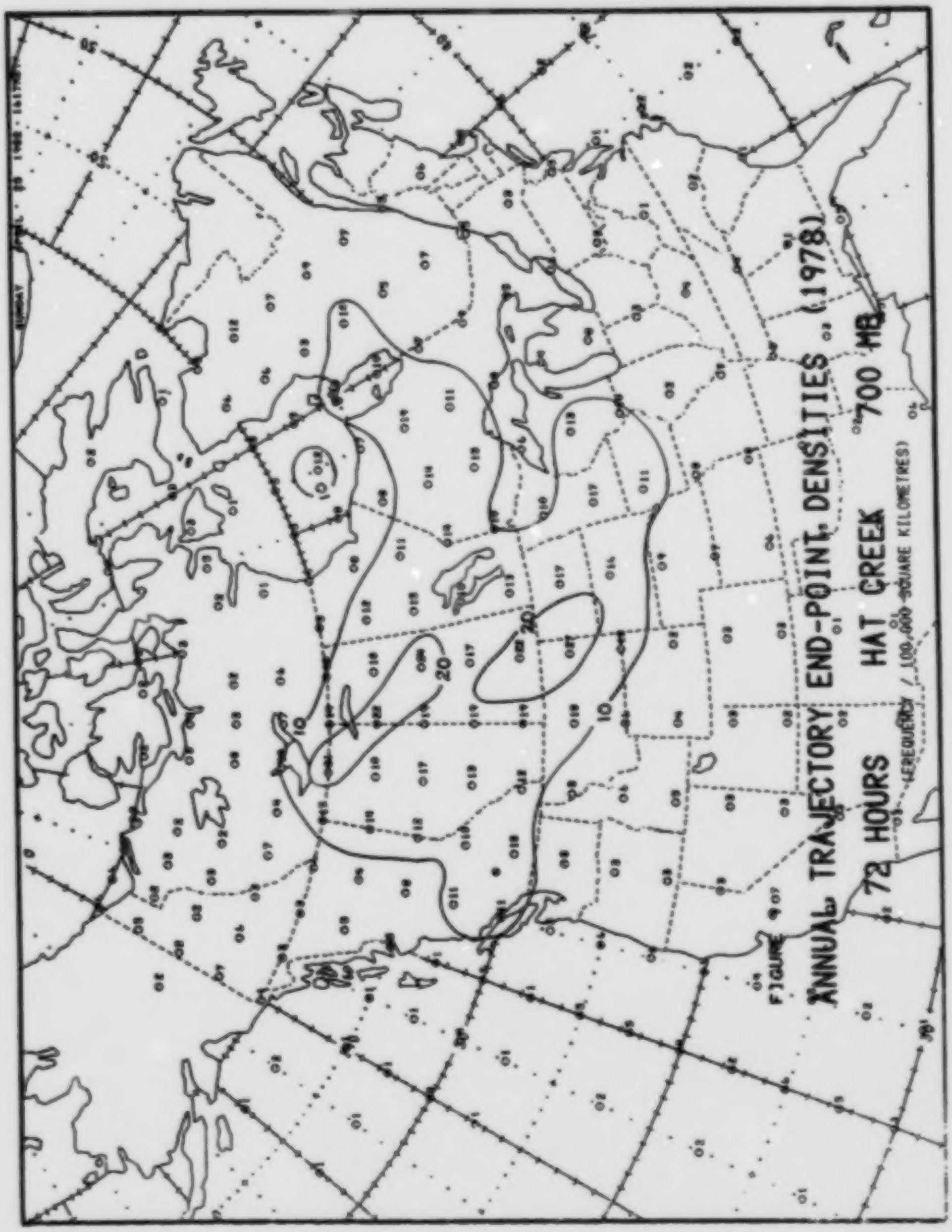


FIGURE 8 ANNUAL TRAJECTORY END-POINT DENSITIES (1978)
48 HOURS HAT CREEK 700 MB

(FREQUENCY / 100,000 SQUARE KILOMETRES)
25
30



FIGURE

ANNUAL TRAJECTORY END-POINT DENSITIES (1978)

72 HOURS HAT CREEK 700 MB

(FREQUENCY / 100,000 SQUARE KILOMETRES)

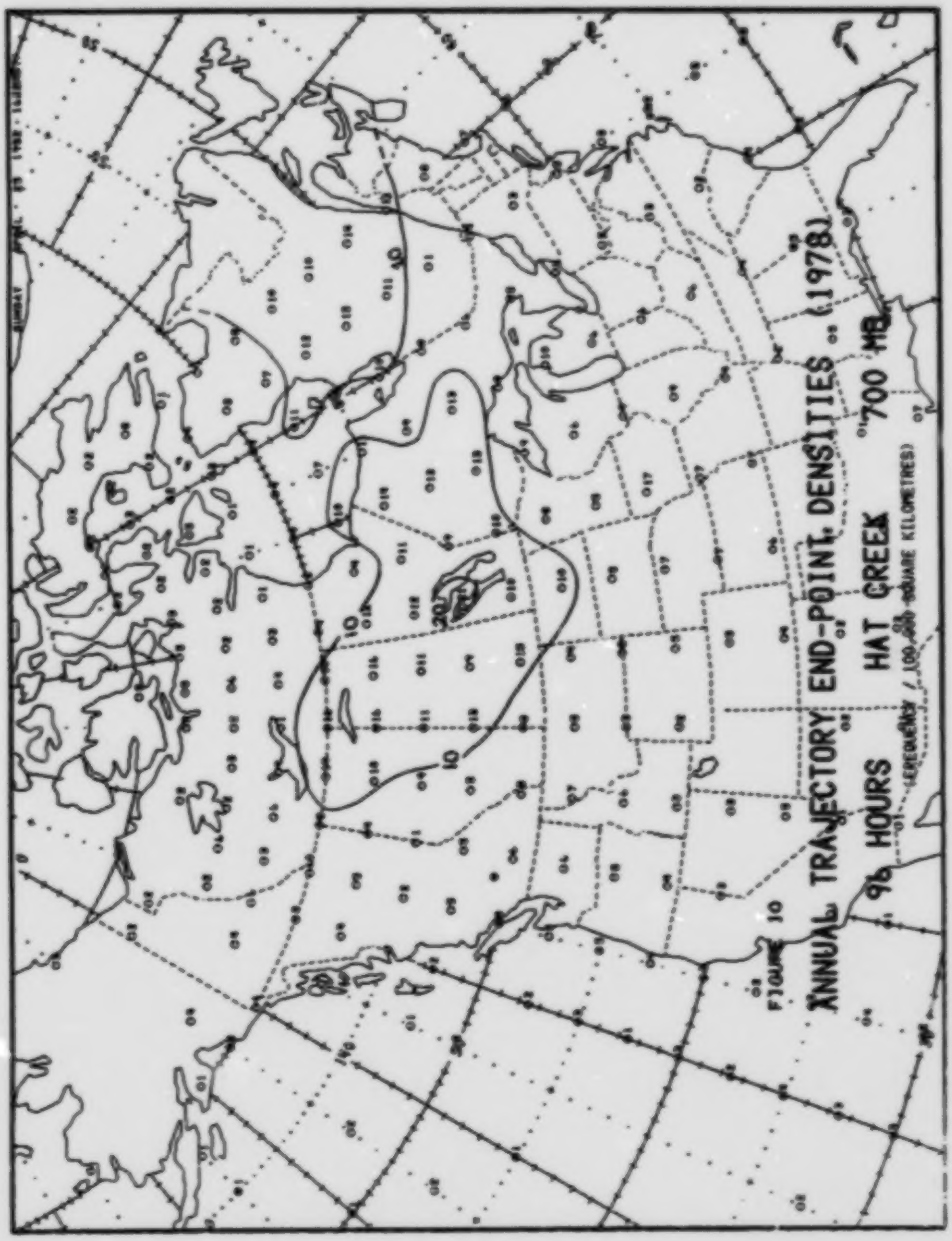


FIGURE 10 ANNUAL TRAJECTORY END-POINT DENSITIES (1978)

96 HOURS HAT CREEK 700 MB

(FREQUENCY / 100,000 SQUARE KILOMETRES)

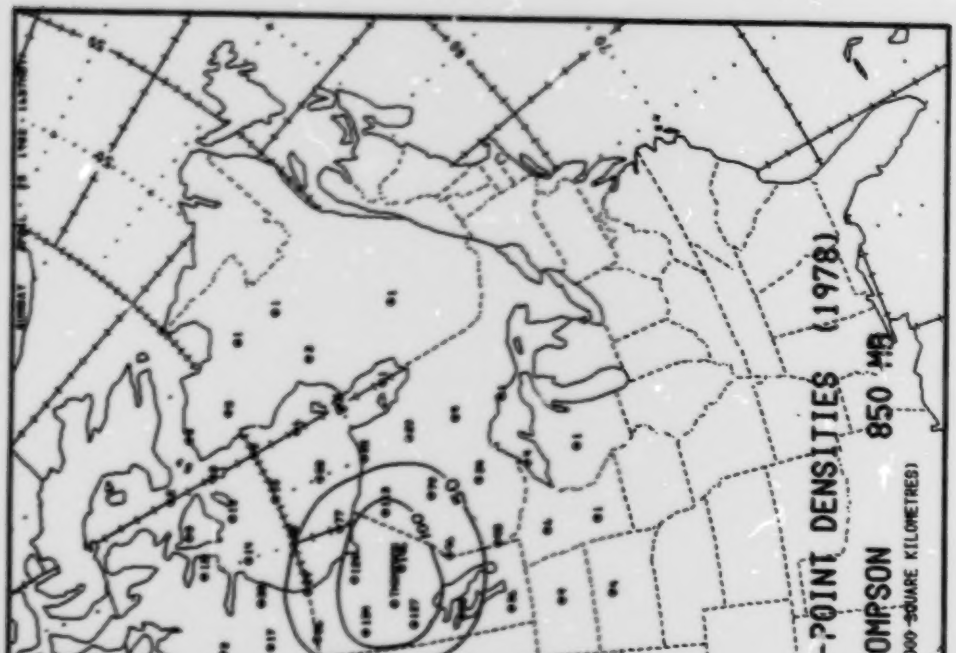


FIGURE 11

ANNUAL TRAJECTORY END-POINT DENSITIES (1978)

24 HOURS THOMPSON 850 MB

(FREQUENCY / 100,000 SQUARE KILOMETRES)

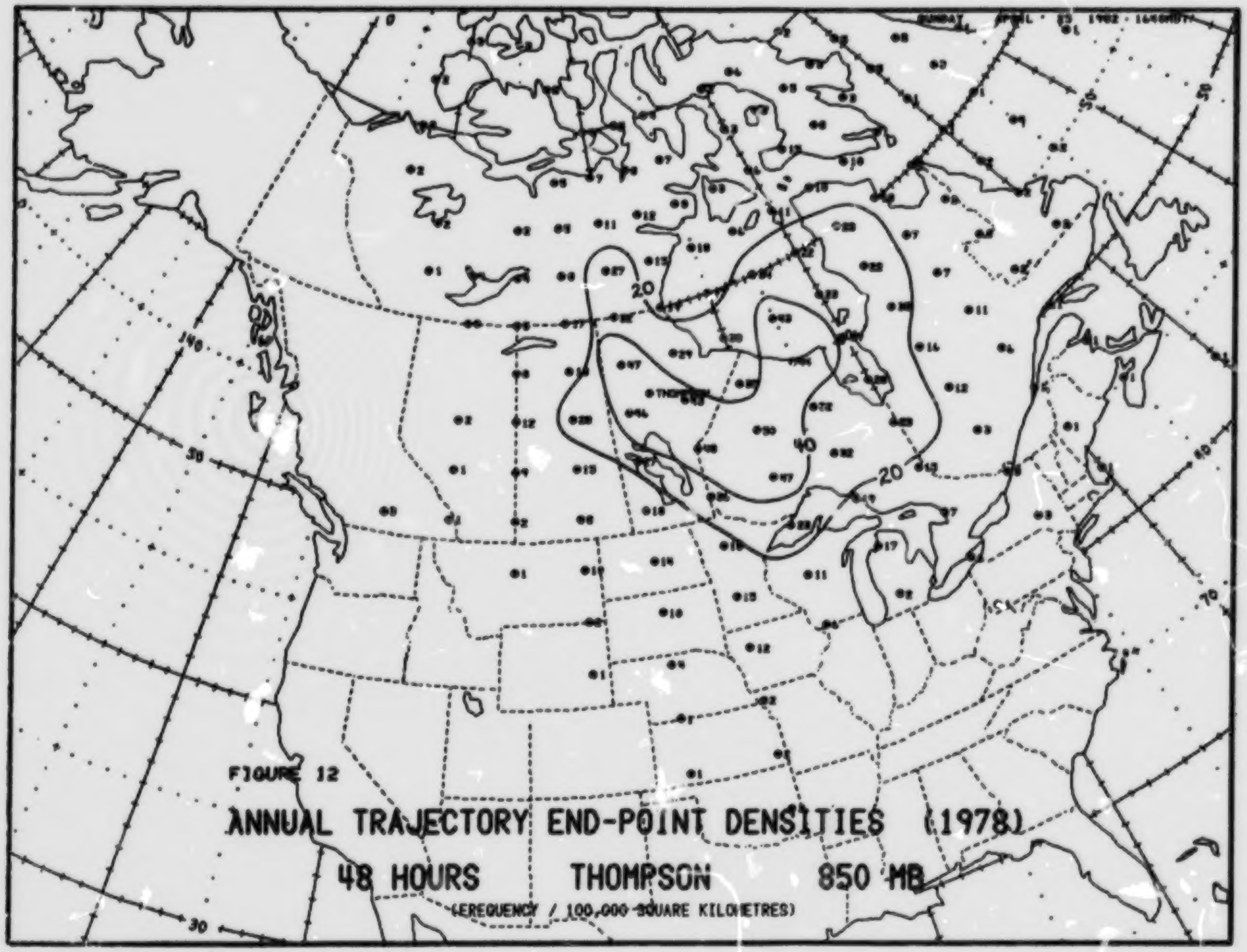

20
40
20
THOMPSON
140
30
70
30

FIGURE 12
ANNUAL TRAJECTORY END-POINT DENSITIES (1978)
48 HOURS THOMPSON 850 MB
(FREQUENCY / 100,000 SQUARE KILOMETRES)

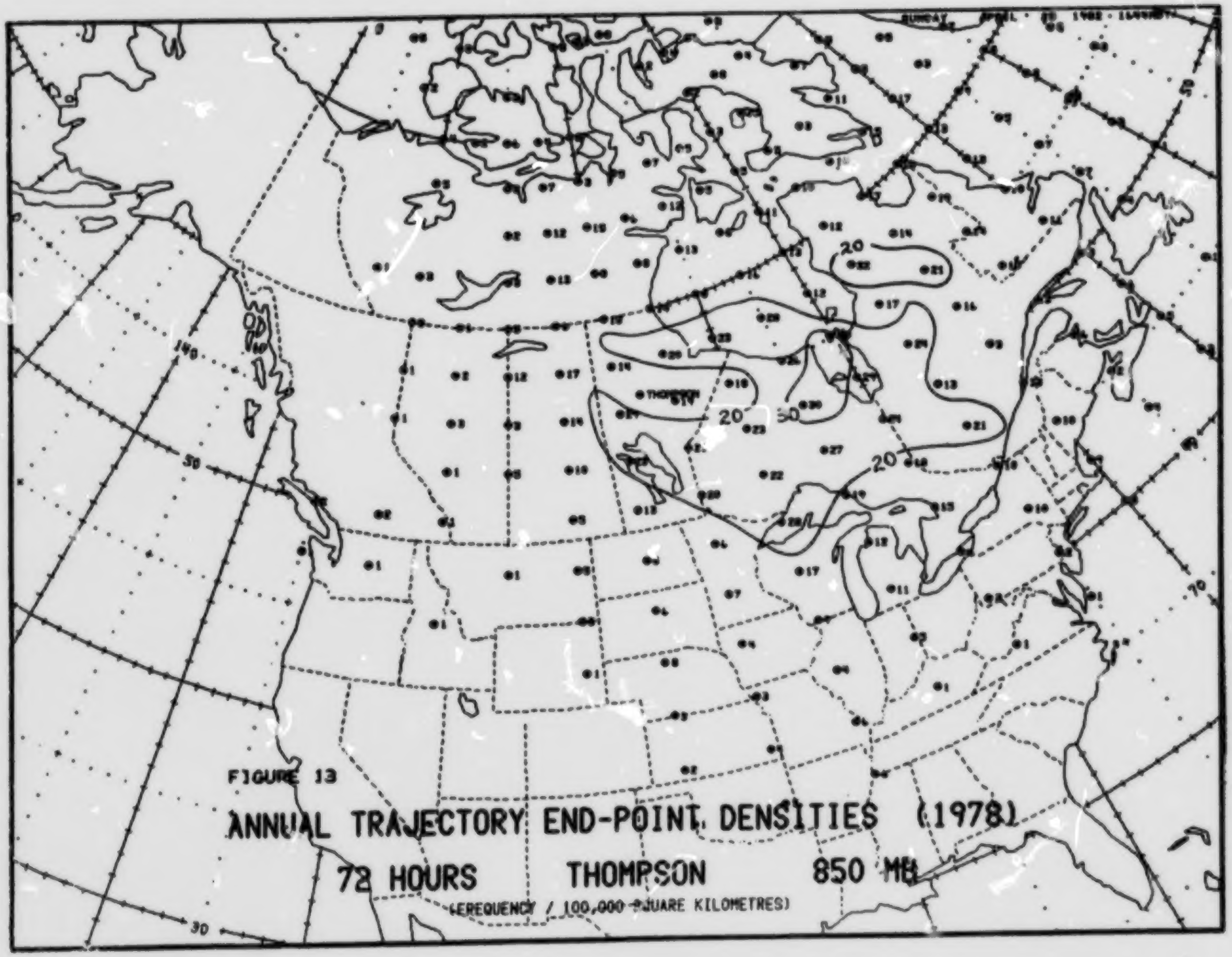

20
THOMPSON
20
30
20
140
30
70
30

FIGURE 13

ANNUAL TRAJECTORY END-POINT DENSITIES (1978)

72 HOURS THOMPSON 850 MB

(FREQUENCY / 100,000 SQUARE KILOMETRES)

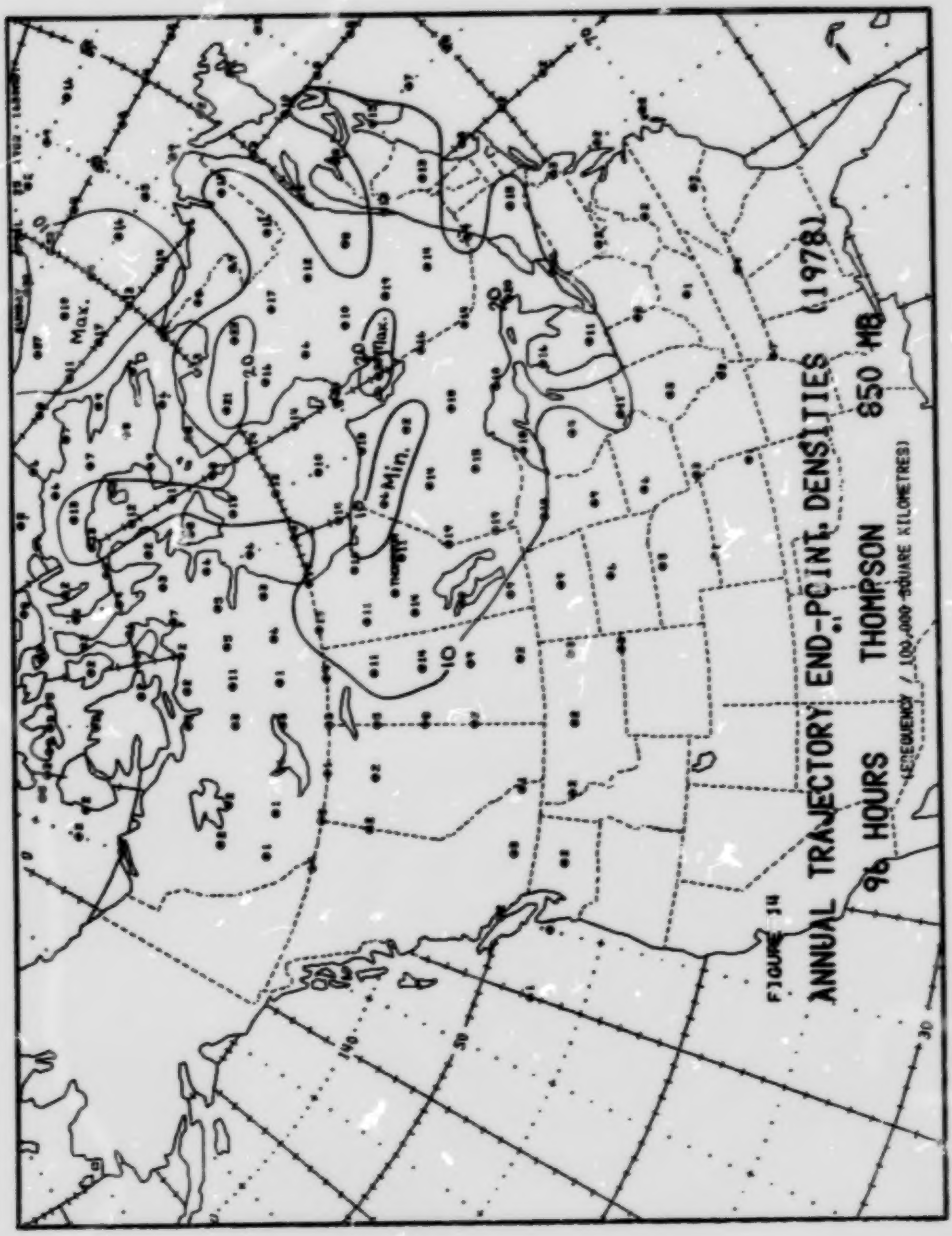


FIGURE 14

ANNUAL TRAJECTORY END-POINT DENSITIES (1978)

96 HOURS THOMPSON 850 MB

(FREQUENCY / 100,000 SQUARE KILOMETRES)

Max.
Max.
Min.
10
20
20
30
50
70

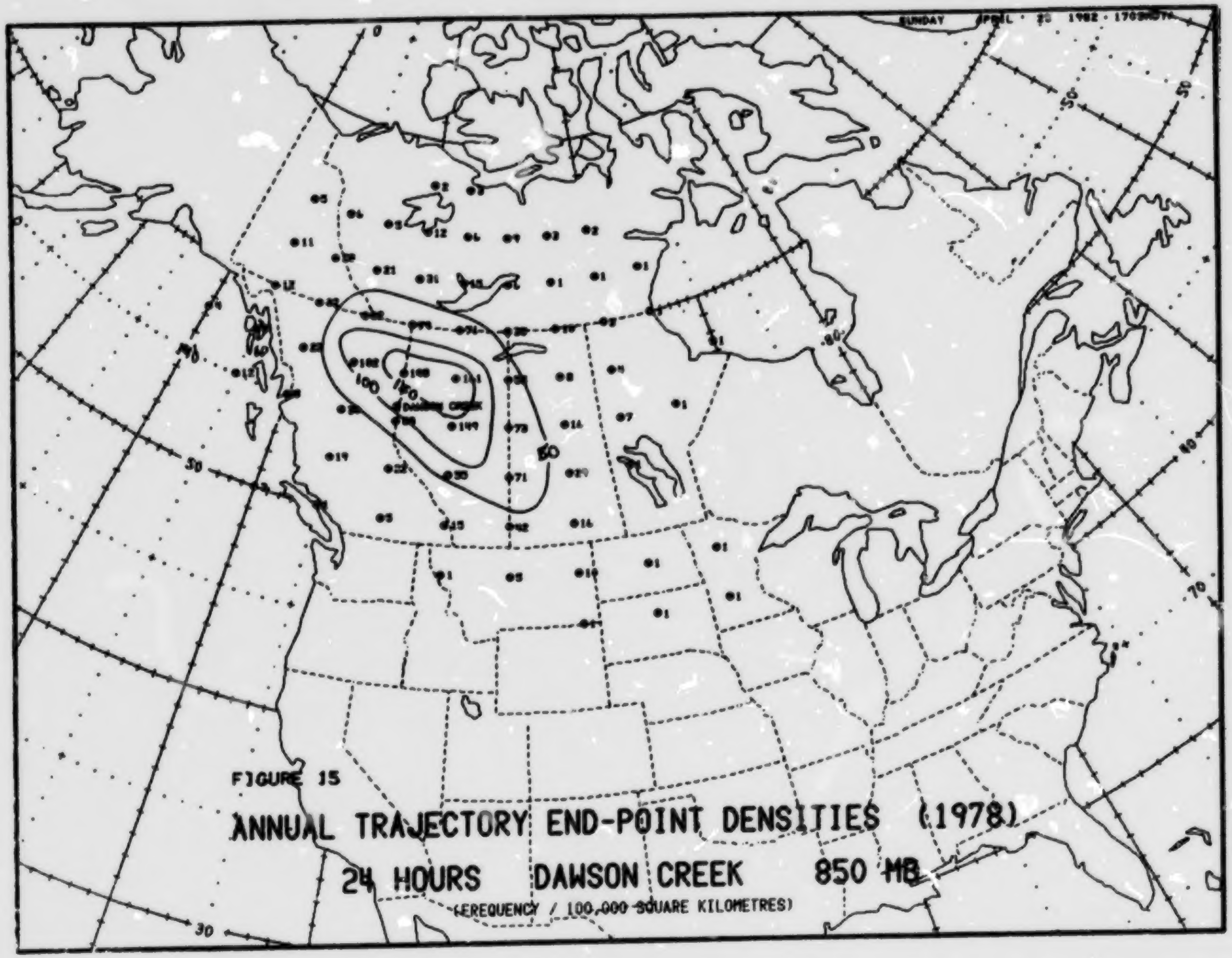

SUNDAY APRIL 25 1982
50
100
150
DAWSON CREEK
30
50
60
70
80

FIGURE 15

ANNUAL TRAJECTORY END-POINT DENSITIES (1978)

24 HOURS DAWSON CREEK 850 MB

(FREQUENCY / 100,000 SQUARE KILOMETRES)

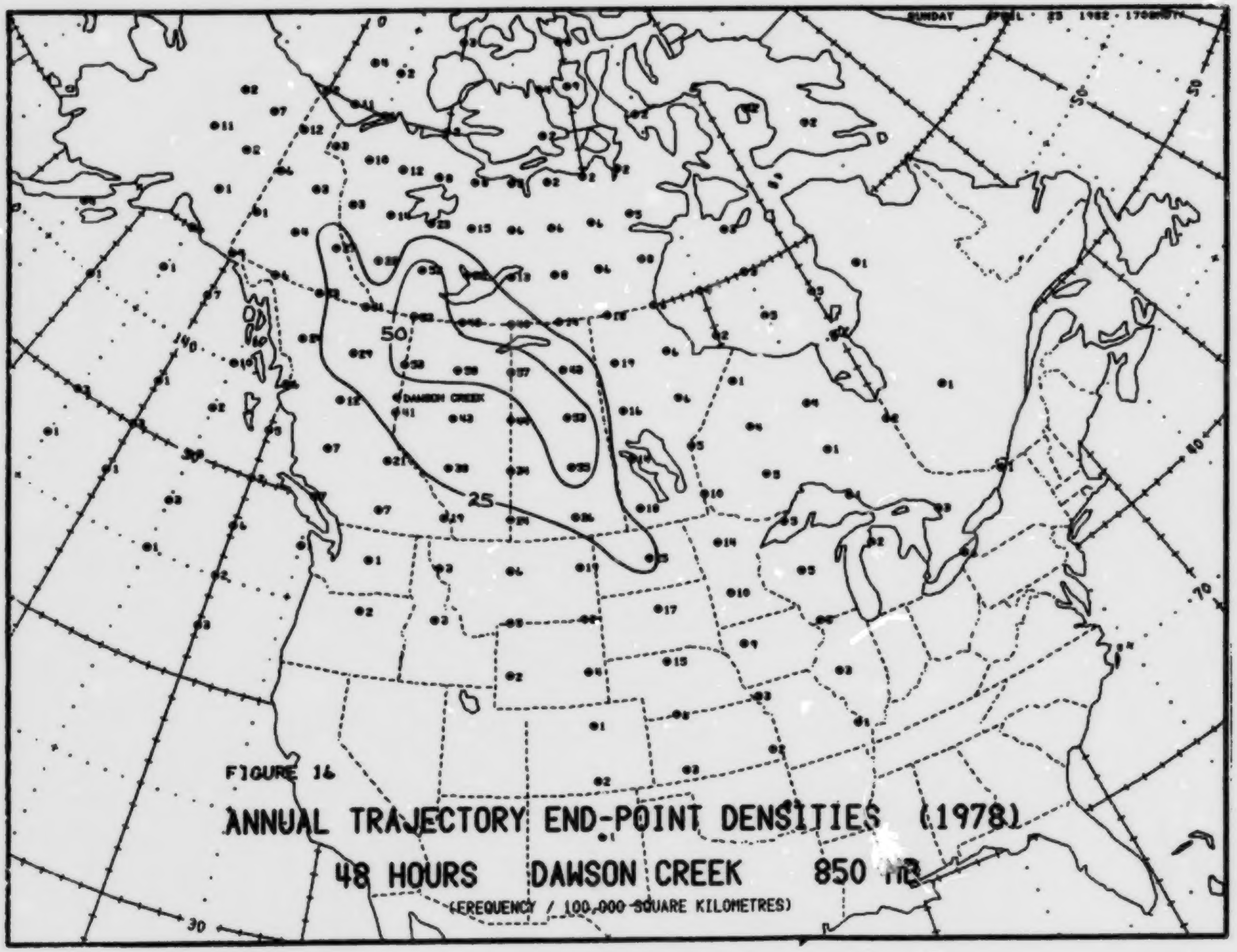
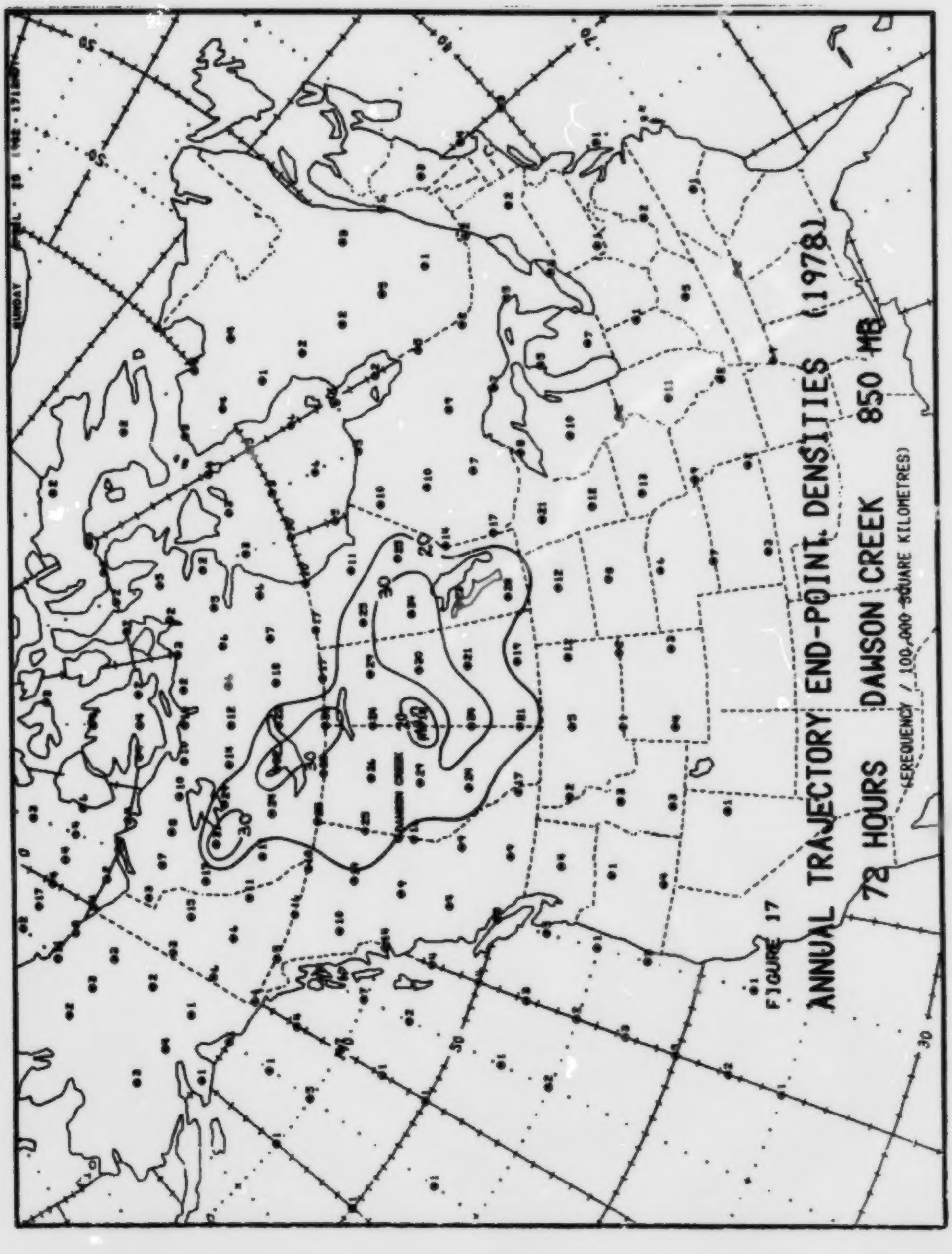

SUNDAY APRIL 25 1982 1700
DAWSON CREEK
50
25
140
30
50
60
70
30

FIGURE 16

ANNUAL TRAJECTORY END-POINT DENSITIES (1978)

48 HOURS DAWSON CREEK 850 MB

(FREQUENCY / 100,000 SQUARE KILOMETRES)



30
20
30
20
30
70
30

FIGURE 17

ANNUAL TRAJECTORY END-POINT DENSITIES (1978)

72 HOURS DAWSON CREEK 850 MB

(FREQUENCY / 100,000 SQUARE KILOMETRES)

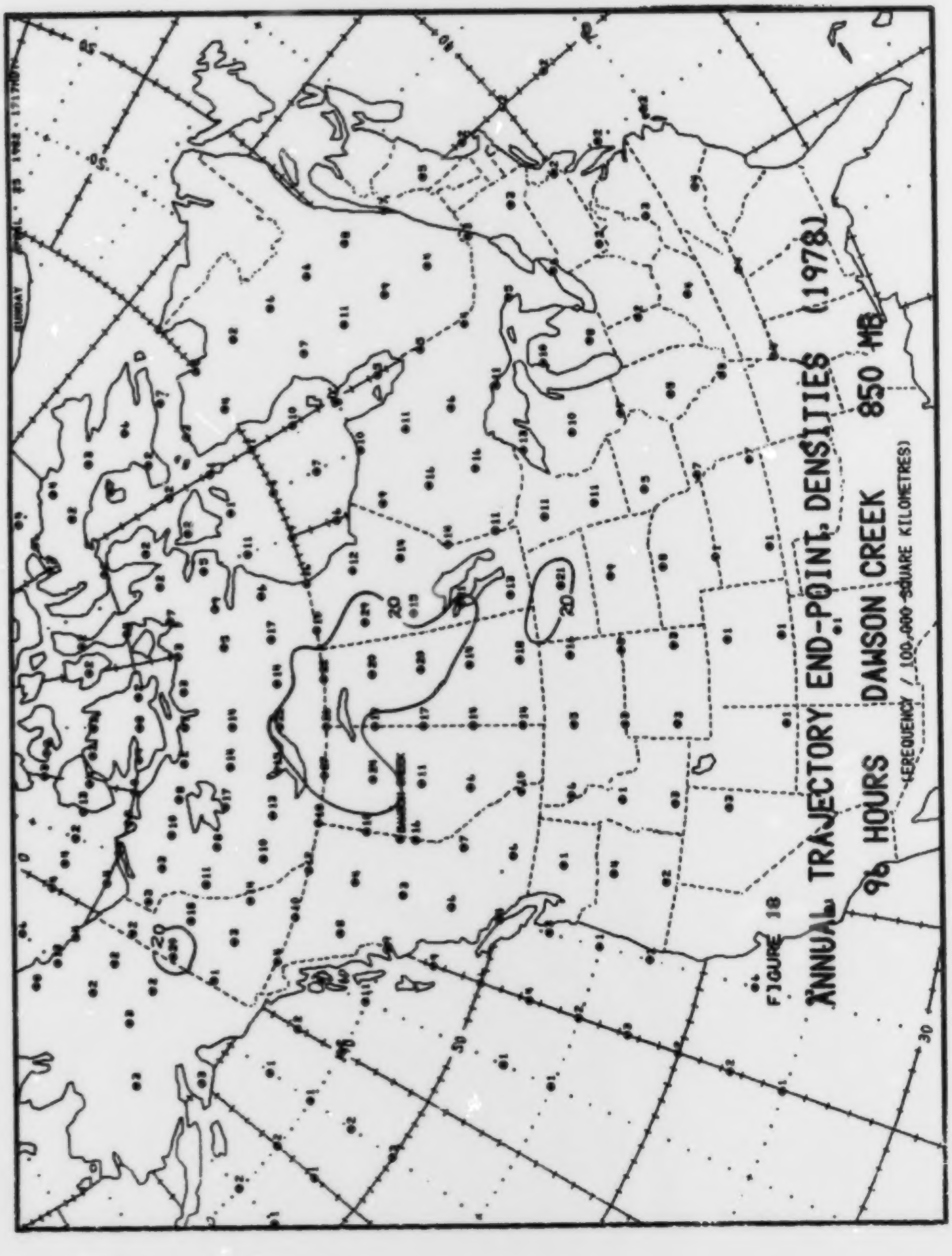


FIGURE 18

ANNUAL TRAJECTORY END-POINT DENSITIES (1978)

96 HOURS DAWSON CREEK 850 MB

(FREQUENCY / 100,000-SQUARE KILOMETRES)

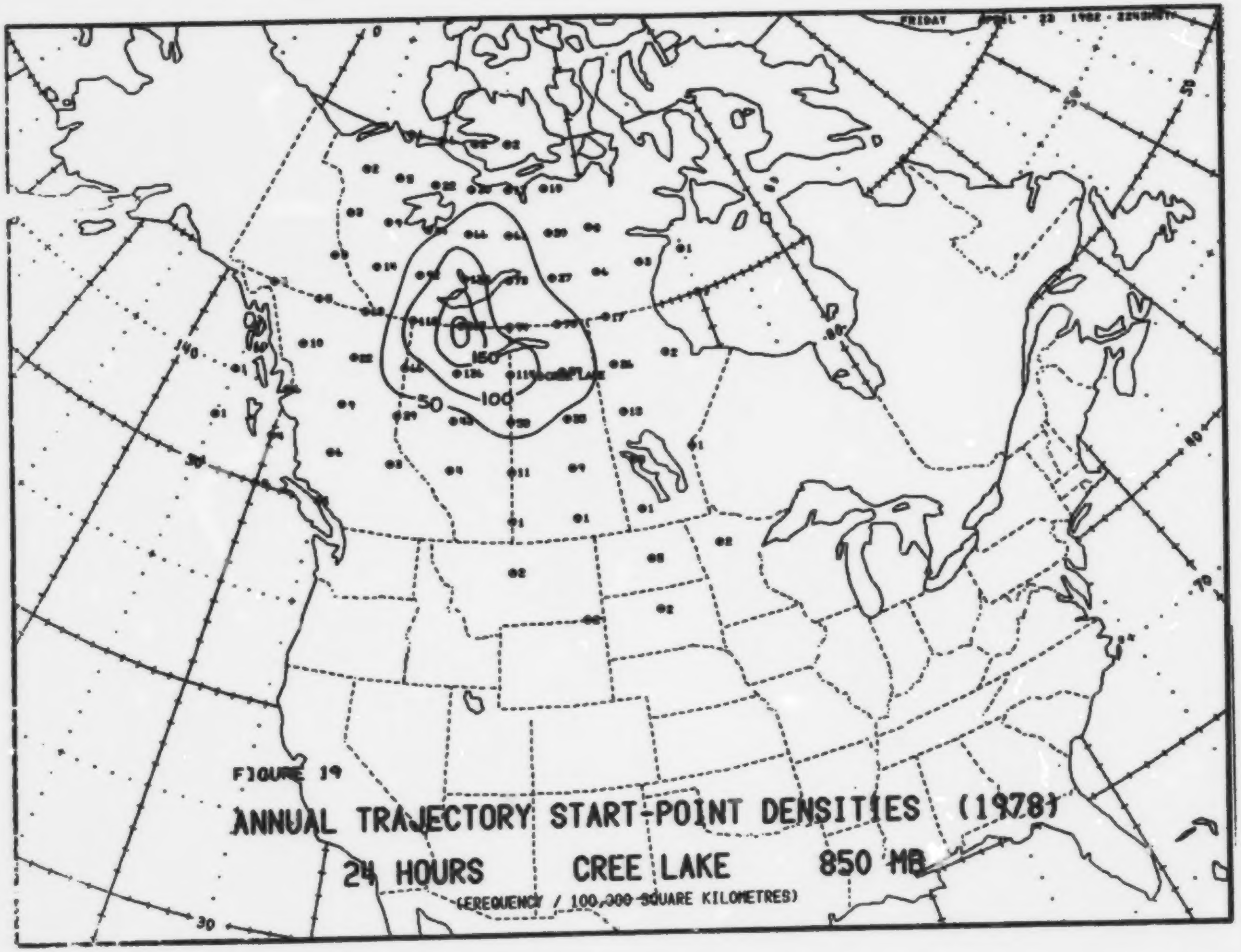

50
100
150
140
30
50
60
70
80
30

FIGURE 19

ANNUAL TRAJECTORY START-POINT DENSITIES (1978)

24 HOURS CREE LAKE 850 MB

(FREQUENCY / 100,000 SQUARE KILOMETRES)

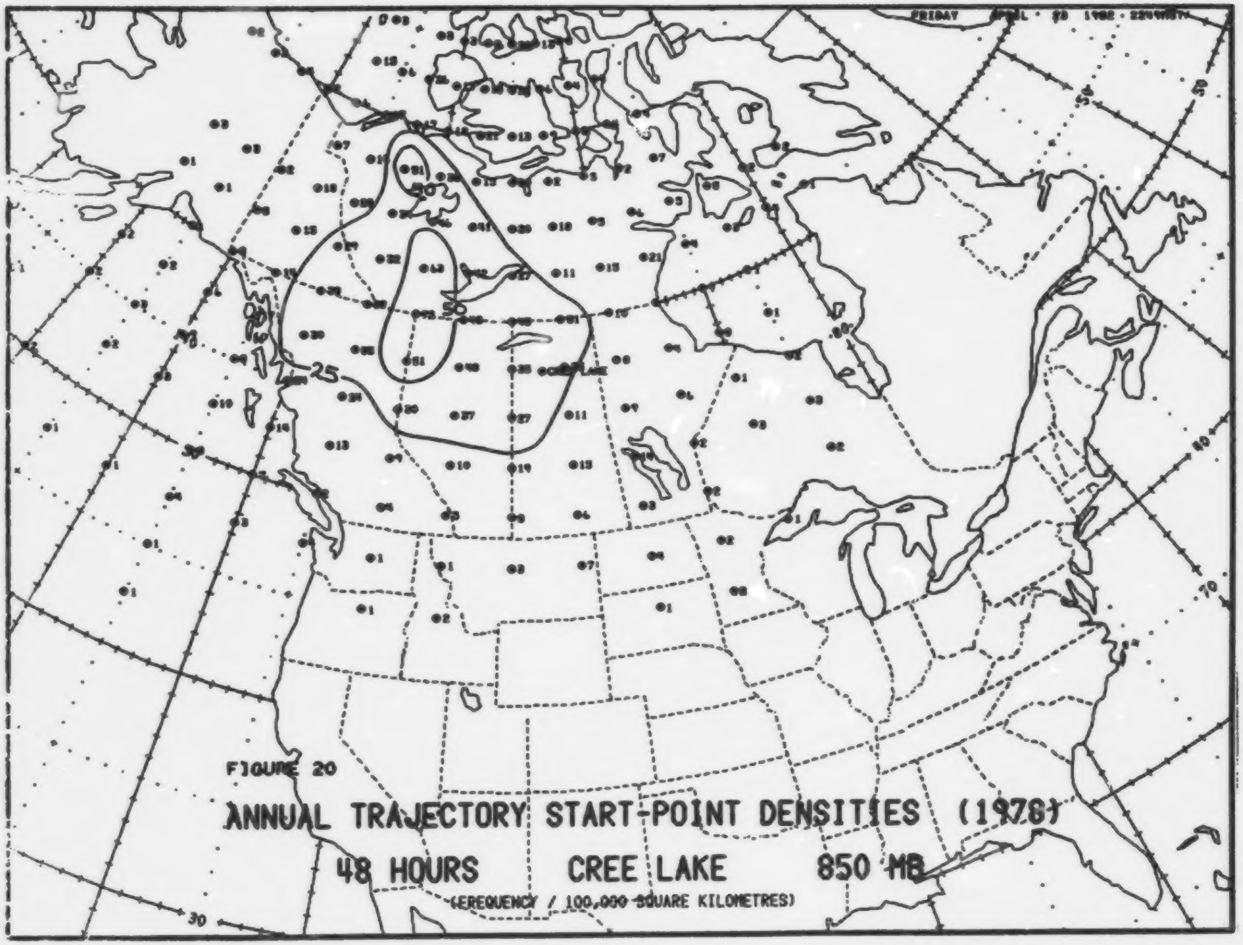


FIGURE 20

ANNUAL TRAJECTORY START-POINT DENSITIES (1978)

48 HOURS CREE LAKE 850 MB

(FREQUENCY / 100,000 SQUARE KILOMETRES)

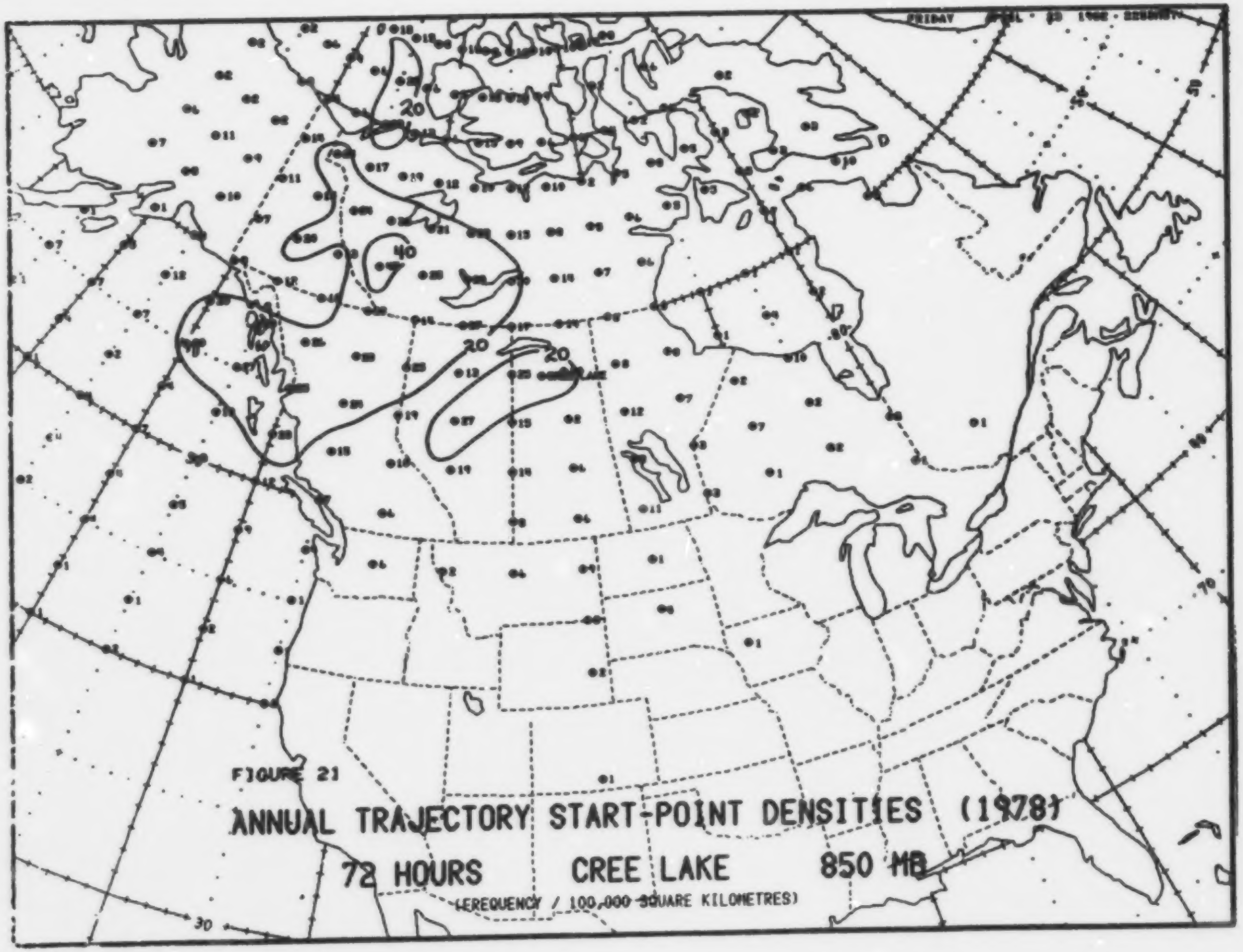

20
40
20
20
20
30
70

FIGURE 21

ANNUAL TRAJECTORY START-POINT DENSITIES (1978)

72 HOURS CREE LAKE 850 MB

(FREQUENCY / 100,000 SQUARE KILOMETRES)

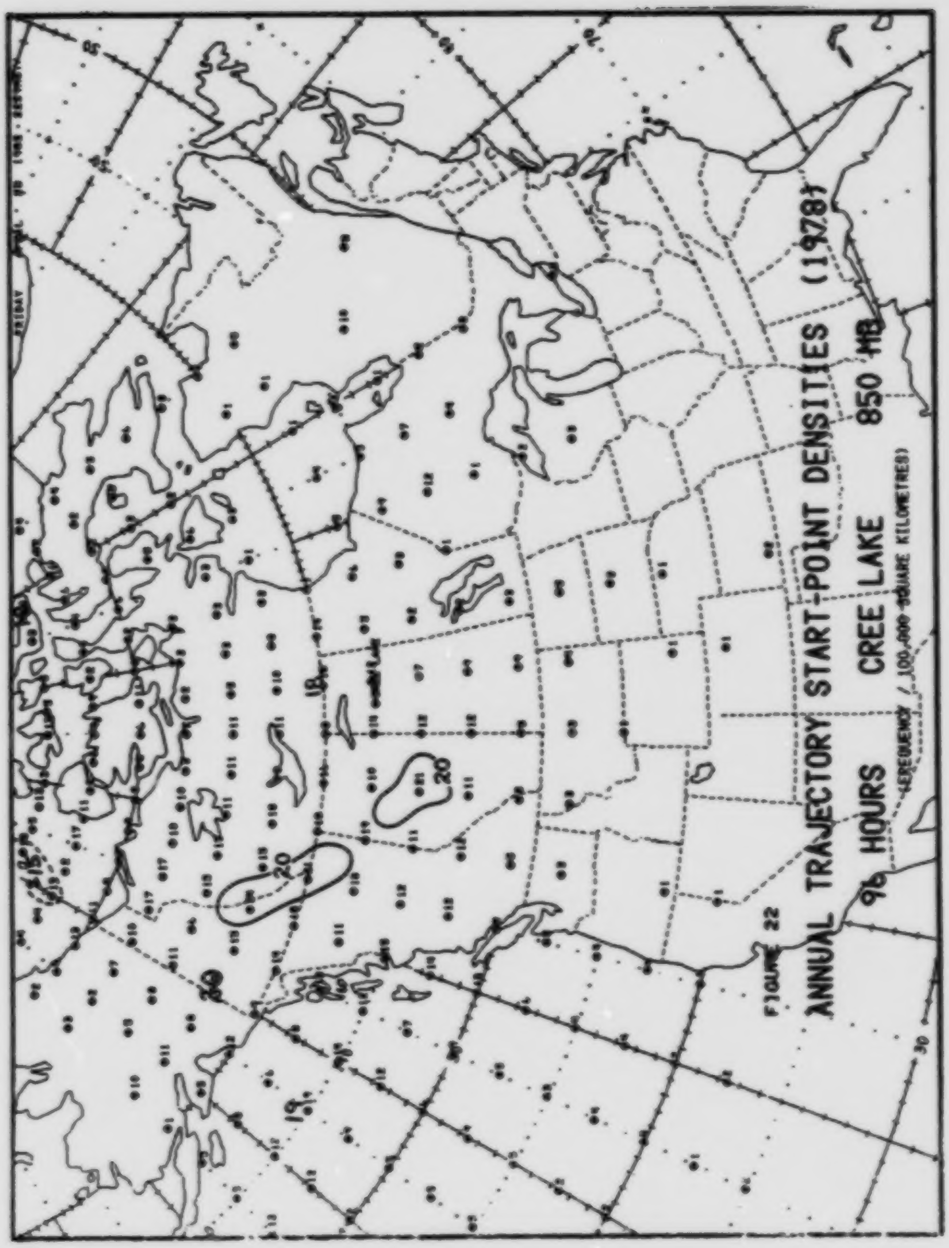


FIGURE 22

ANNUAL TRAJECTORY START-POINT DENSITIES (1978)

96 HOURS CREE LAKE 850 MB

(FREQUENCY / 100,000 SQUARE KILOMETRES)

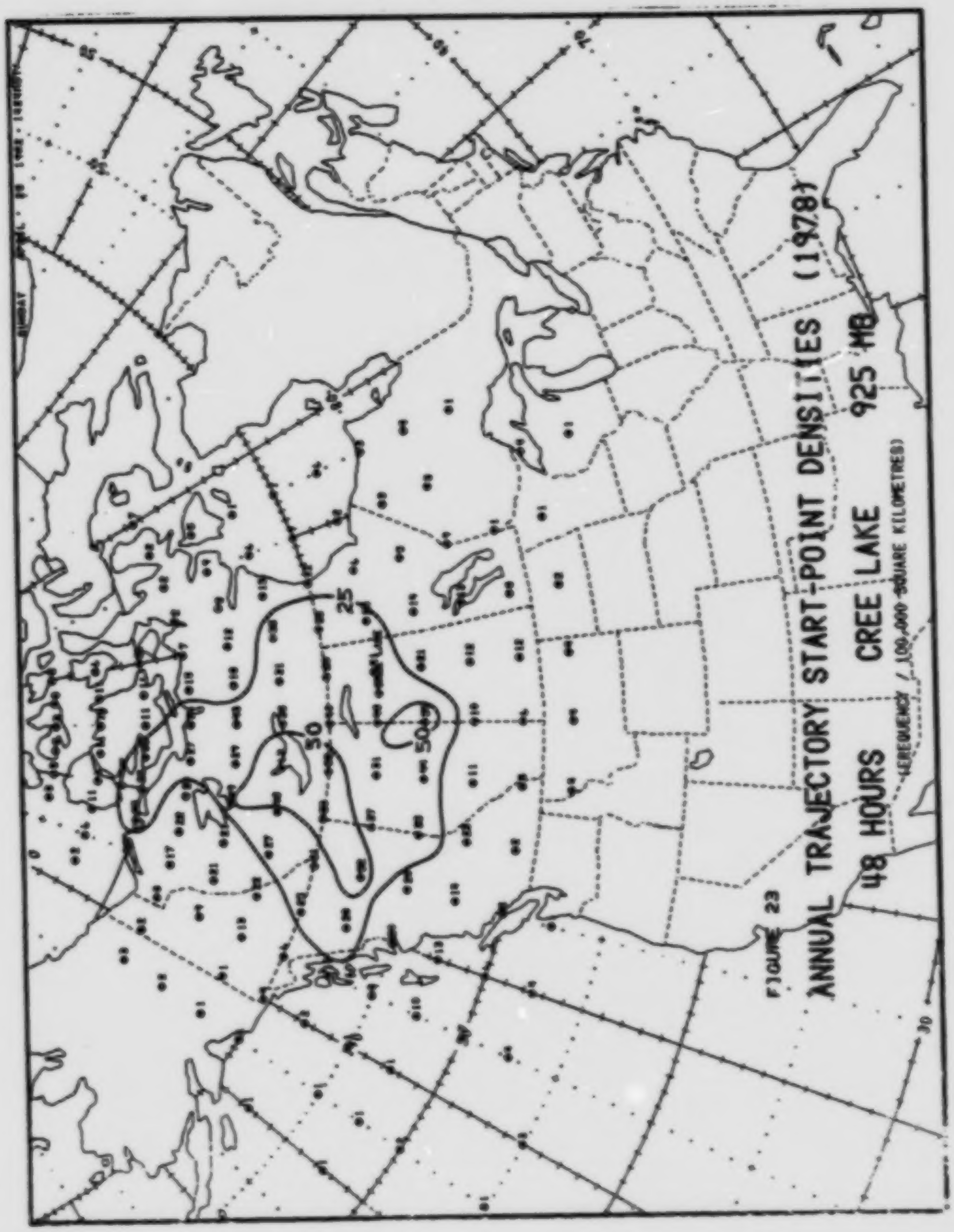


FIGURE 23

ANNUAL TRAJECTORY START-POINT DENSITIES (1978)

48 HOURS CREE LAKE 925 MB

(FREQUENCY / 100,000 SQUARE KILOMETRES)

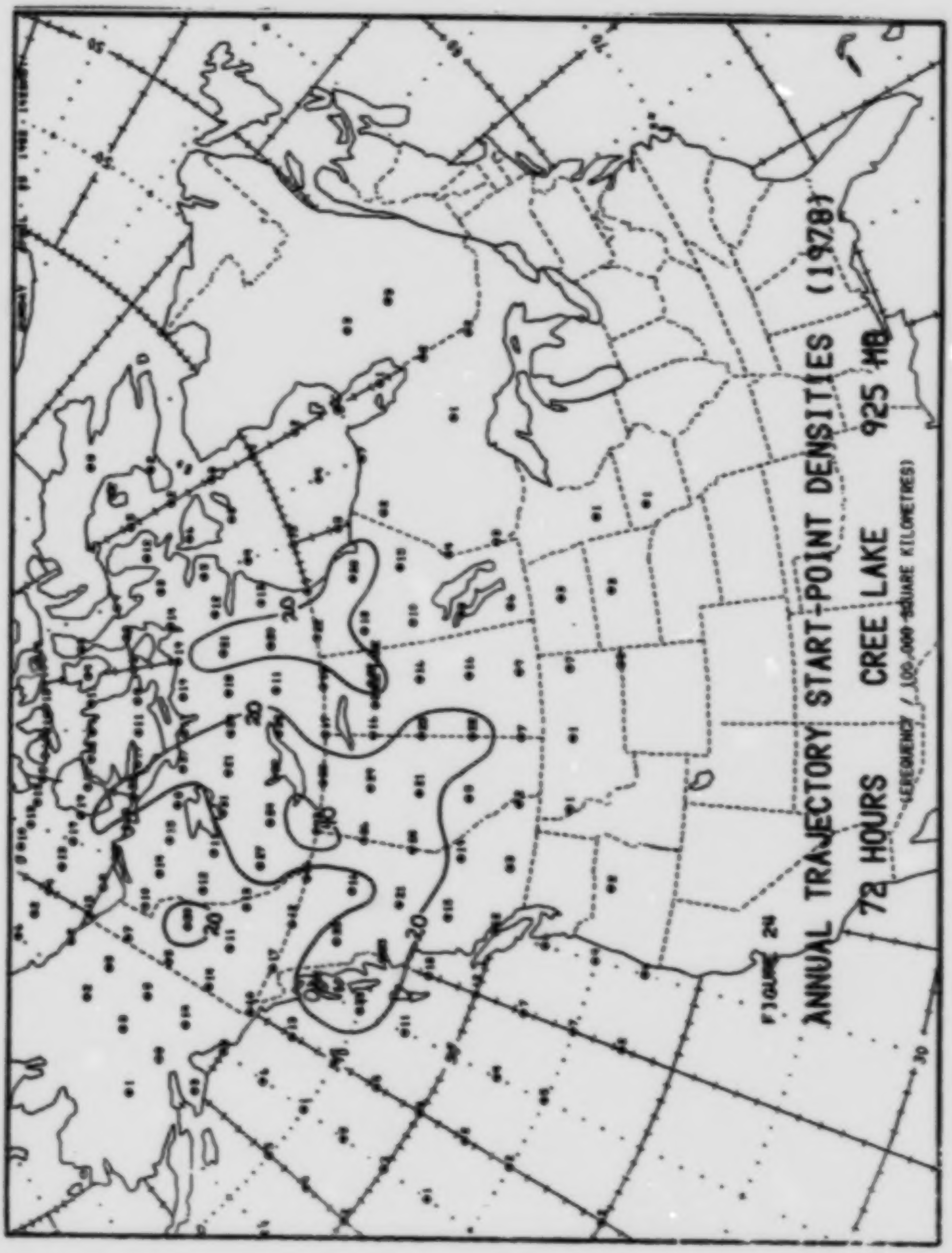
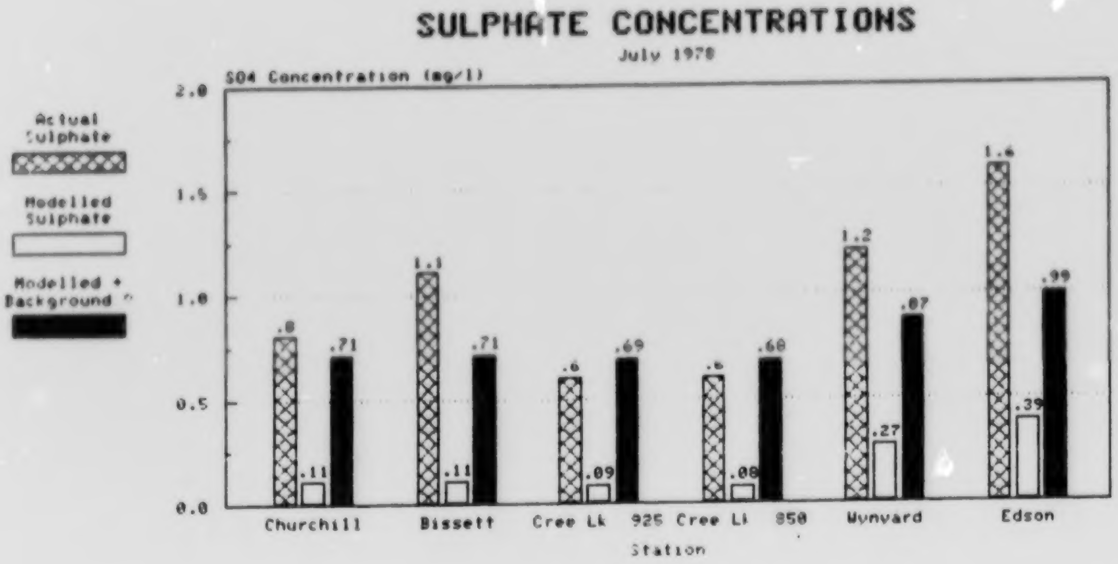

20
20
20
20
20
20
30

FIGURE 24

ANNUAL TRAJECTORY START-POINT DENSITIES (1978)

72 HOURS CREE LAKE 925 MB

(FREQUENCY / 100,000 SQUARE KILOMETRES)



SULPHATE CONCENTRATIONS

July 1978

FIGURE 25

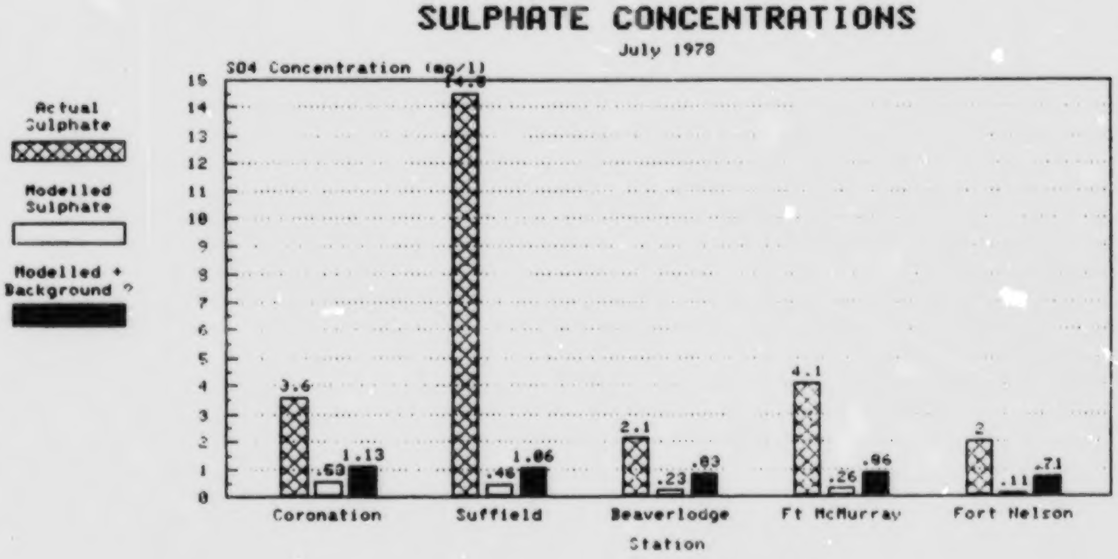

SULPHATE CONCENTRATIONS
July 1978
SO4 Concentration (mg/l)
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
Actual Sulphate
Modelled Sulphate
Modelled + Background ?
3.6
.53
1.13
14.6
.46
1.06
2.1
.23
.83
4.1
.26
.86
2
.11
.71
Coronation
Suffield
Beaverlodge
Ft McMurray
Fort Nelson
Station

FIGURE 26

A MEASUREMENT SYSTEM FOR SO_2 DRY DEPOSITION RATES

J.E. HUNT[1], R.G. WRIGHT[1], R.L. DESJARDINS[2]

Abstract

In Alberta it is likely that the most important atmospheric removal process for SO_2 is dry deposition. There are, however, inadequate data to allow a quantitative assessment and modeling of this process which can properly incorporate expected variations in governing parameters. Ten methods to experimentally measure SO_2 deposition rates are briefly reviewed with respect to their basic features and evaluated against a set of criteria for the suitability of each technique to produce data from which generalized relationships between deposition velocities and other more easily measured parameters can be derived. These methods fall into three basic categories: atmospheric flux, mass balance and surface accumulation techniques. Of these only the atmospheric flux methods were judged suitable from which eddy accumulation and concentration gradient profile methods were selected for further study. Development of an SO_2 continuous monitor using flame photometric detection with enhanced sensitivity by SF_6 addition is described. This technique improved sensitivity by a factor of 25 for a detection limit of about 0.04 ppb. A preliminary field study is described in which both techniques were used. The eddy accumulation method required some modification due to the lack of suitable storage containers which could accumulate samples without surface losses prior to chemical analysis. The modifications lead to unacceptably large sample dilutions (a factor of about 20) and further development of the sampling system is required. The concentration gradient profile method produced reasonable results for deposition velocities at the study site although very low SO_2 concentrations (1.0 to 1.5 ppb) limited the accuracy of the data.

[1] Concord Scientific Corporation, Toronto, Ontario
[2] Canadian Department of Agriculture, Ottawa, Ontario

1. INTRODUCTION

In Alberta, anthropogenic emissions of SO_x, reduced sulfur compounds and NO_x are the main precursors of acid forming atmospheric pollutants. Sulfur emissions are mainly in the form of SO_2. Once emitted to the atmosphere these compounds are subject to atmospheric dispersion, transport, and chemical and physical transformations. Removal from the atmosphere takes place by both wet and dry deposition mechanisms. The efficiency of these processes is dependent on a variety of factors such as prevailing meteorological conditions, topographical features, and the chemical and physical properties of the pollutants and absorbing surfaces. It is probable that, for most areas of Alberta, dry deposition is the most important atmospheric removal process for SO_2 (Department of Environment, Alberta 1978). There are, however, inadequate data to allow a quantitative assessment and modeling of SO_2 dry deposition in Alberta to be carried out which would properly incorporate expected variations under various conditions.

A large number of studies reported in the literature have measured the dry deposition of SO_2 using a variety of methods. These have been reviewed extensively by Denison et al. (1979) and Sehmel (1980). In general, literature data do not allow prediction of deposition rates to be expected for conditions different from those under which the measurements were made. This is due to either the failure of these studies to measure or report the major parameters which affect deposition rates, or the use of methods which are inherently incapable of allowing for the discrimination of the effects of these determining parameters. The rate of SO_2 dry deposition is a function of atmospheric stability, surface roughness, wind speed, type and condition of vegetation, crop wetness, and soil moisture content and pH. It is important to understand the functional relationships between SO_2 dry deposition rates and these variables if a realistic description is to be obtained which is adequate for numerical simulations of the transport, fate and effect of emitted SO_2. At the present time these relationships are not well understood.

In his keynote address presented during a workshop on dry deposition (Argonne National Laboratory, December, 1979), Paul Frenzen commented that "... the useful tendency for new scientific principles is to clear away masses of inconclusive experimental observations. Since Newton formulated the law of gravity, we need no longer measure the fall of every apple!" This comment certainly applies to the current understanding of SO_2 dry deposition. There is a need for methodology development and measurement programs capable of providing suitable data from which functional relationships can be derived between SO_2 dry deposition and other more easily measured parameters.

In recognition of this need the Alberta Department of Environment is supporting a program to study SO_2 dry deposition. The ultimate objective is to develop and demonstrate a field operational methodology to determine, within known confidence limits, the dry deposition of SO_2 on bare soil and one crop in the vicinity of a sour gas plant. The first phase, now completed, was a review and analysis of possible experimental techniques which could be used to measure the dry deposition of SO_2 (Hunt et al. 1981).

This presentation briefly reviews the results of the first phase and describes progress to date on the second phase of the program which is the laboratory development and field testing of two promising experimental methodologies for the measurement of SO_2 dry deposition.

2. DEPOSITION VELOCITY AND TRANSFER RESISTANCE

The concepts of deposition velocities and transfer resistance are frequently used in reference to dry deposition rates of SO_2. These parameters are useful since they directly link ambient concentrations with deposition fluxes. In order to provide a general background with which the measurement methodologies are assessed, a brief discussion of these concepts is presented in this Section.

Mass transfer of SO_2 can be considered as taking place across resistance elements in series. These are the turbulent atmospheric layer, the viscous laminar atmospheric sub-layer and finally the surface sorption element itself. In the constant flux layer the SO_2 deposition flux will be the same across each resistive element and will be determined by the combined resistances to gas transfer for all elements. A theoretical basis for the concepts and relationships between deposition flux density, deposition velocity and transfer resistance have been given by Hicks (1976); Bolin et al. (1974); Chamberlain (1975); Wesely and Hicks (1976); and Garland (1977). These have been summarized recently by Denison et al. (1979).

Under most conditions, where the concentration of SO_2 is not too high, it is generally considered that the rate of sorption at the surface may be expected to be proportional to the concentration immediately adjacent to the surface. Thus, the surface flux of SO_2 can be written

$$F = \frac{C_s}{R_s} \tag{1}$$

where F = flux density to the surface

C_s = concentration immediately adjacent to the surface

R_s = proportionality constant usually referred to as the surface resistance

The surface, or canopy, resistance R_s, is determined by the different sinks for SO_2 acting together. For example, for a simple vegetative canopy comprising one layer of uniform vegetation above bare soil there are three sites of the surface for absorption - the sub-stomatal cavity, the leaf cuticle, and the soil surface. These can be considered as resistances in parallel such that

$$\frac{1}{R_s} = \frac{1}{R_{s_1}} + \frac{1}{R_{s_2}} + \frac{1}{R_{s_3}} \qquad (2)$$

Although some attempts have been made to model R_s, (Denison et al. 1979), it is dependent on the nature and condition of the surface. There is inadequate information and understanding of the governing parameters and R_s is often found by the difference between the measured total and aerodynamic resistances.

The exchange of SO_2 between the atmosphere and the surface (soil, vegetation or water, etc.) is governed by transfer through the atmospheric surface boundary layer as well as sorption at the surface. Transfer of SO_2 in the atmosphere in the vertical direction is often modelled by the use of flux-gradient relationships. The downward flux is parameterized in terms of the so-called K-theory by

$$F(z) = K(z)\ \frac{dC\,(z)}{dz} \qquad (3)$$

where K(z) = diffusion coefficient

C(z) = concentration at height z from the surface

Equation (3) is identical in form to that describing molecular diffusion where K(z) is replaced by the molecular diffusion coefficient. Close to the surface, in the laminar atmospheric sub-layer, viscous drag impedes mixing, and transport is determined primarily by molecular diffusion. At greater heights, mixing by atmospheric turbulent eddies dominates over molecular diffusion and the turbulent eddy diffusion coefficient for the parameter of interest is used in Equation (3).

Integration of Equation (3) gives

$$\int_0^z \frac{F(z)}{K(z)} dz = C(z) - C_s \tag{4}$$

The vertical flux of SO_2 will generally be height dependent. However, under conditions where the flow is well adjusted to the underlying surface (i.e., there is no horizontal flux divergence), then the flux may be considered to be constant with height. This requires a fetch of uniform suface extending upwind at least 100 to 200 times the height for which a constant flux is assumed. Under these conditions, Equation (4) becomes

$$F = \frac{C(z) - C_s}{R_g(z)} \tag{5}$$

where

$$R_g(z) = \int_0^z \frac{dz}{K(z)} \tag{6}$$

The quantity $R_g(z)$ is the atmospheric resistance to transfer from height z to the surface. From Equation (2) and (5)

$$F = \frac{C(z)}{R_s + R_g(z)} \tag{7}$$

Thus, the total resistance to deposition from height z is

$$R(z) = R_s + R_g(z) \tag{8}$$

The deposition rate is frequently discussed in terms of the deposition velocity, $V_g(z)$, where

$$F = V_g(z)\, C(z) \tag{9}$$

and therefore from Equation (7) and (8)

$$V_g(z) = \frac{1}{R(z)} \tag{10}$$

The atmospheric transfer resistance $R_g(z)$ can be divided into

$$R_g(z) = R_a(z) + R_b \tag{11}$$

where $R_a(z)$ = the aerodynamic resistance in which turbulent eddy diffusion dominates

R_b = the atmospheric viscous sub-layer resistance in which molecular diffusion is more important than eddy diffusion.

In the above formulation, flux determination depends on a knowledge of concentration gradients and diffusivities. The eddy diffusivity of SO_2 is unknown generally, but at practical measurement heights turbulent transport completely dominates molecular processes. Consequently, the diffusivities of all trace gases are expected to be the same.

3. DRY DEPOSITION MEASUREMENT METHODOLOGIES

There are at least ten different methods reported or suggested which can be used to determine dry deposition rates of SO_2 from the atmosphere. These are conveniently divided into three basic categories.

Atmospheric Flux Measurements:
- eddy correlation
- variance correlation
- eddy accumulation
- concentration gradient

Mass Balance:
- atmospheric budget
- watershed budget
- containers (lysimeter)

Surface Accumulation:
- ^{35}S tracer
- $^{34}S/^{32}S$ tracers
- deposition collectors

The following is a very brief description of the basic features of these methods. A more complete description and comparison of methods is available in the Phase I report (Hunt et al., 1981).

3.1 EDDY CORRELATION

The eddy correlation method for the measurement of the vertical transfer of atmospheric properties and constituents was first applied to momentum fluxes by workers in the U.K. using laborious hand calculation methods. Subsequent effort extended the method to include sensible heat and water vapour; (Hicks 1970 ; Yap and Oke 1974). Application of the method to include the measurement of the fluxes of trace atmospheric gases has been demonstrated by Desjardins and Lemon (1974). Fluxes of CO_2, O_3 and fine particles have been reported (Jones and Smith 1977), Wesely et al. 1977). There have not, as yet, been any published measurements of SO_2 dry deposition rates using eddy correlation methods although efforts are being undertaken in this area (Garland 1978 , Hicks 1980 personal communication).

The eddy correlation method assumes that the dominant mechanism in the atmospheric transport of the property of interest is through turbulent eddies. The technique provides a direct measure of vertical flux by correlating the vertical component of wind speed with the instantaneous SO_2 concentration at a given measurement point. Deposition rates are determined by calculating the net vertical flux over a suitable averaging period.

3.2 VARIANCE CORRELATION

The variance correlation method is similar to the eddy correlation approach to measure dry deposition. The variances in vertical wind speed and in SO_2 concentrations are determined over a suitable averaging period. The product of the standard deviations of these parameters and the correlation coefficient between them yields the flux of SO_2. A value for this correlation coefficient is required and estimates have been suggested by Hicks and Wesely (1978).

An alternative approach uses the observation that in the atmosphere turbulent fluctuations of temperature and water vapor concentrations are highly correlated (McBean 1973 , Swinbank and Dyer 1967 , Wesely and Hicks 1978). Hence the correlation coefficients between each of these parameters and vertical wind fluctuations are expected to be approximately equal. Assuming that this similarity can be extended from water vapor to other atmospheric gases then it follows that the ratio of fluxes for SO_2 and sensible heat equals the ratio of their respective standard deviations. This avoids the need to determine vertical wind speeds and the requirement for correlation coefficients. No atmospheric flux measurements using this method have yet been reported in the literature.

3.3 EDDY ACCUMULATION

The development of the eddy accumulation technique was stimulated by a lack of sensors of adequate time response for scalar quantities measured in eddy correlation methods. The method is similar to eddy correlation except that the need for fast response chemical sensors is sidestepped by the continuous accumulation of air samples during the measurement period for later analysis. The method was first seriously considered in the middle 1960's but successful application for gases was not achieved until recent work by Desjardins (1980-unpublished).

The theoretical basis for the method has been reported by Desjardins (1977). It is assumed that the dominant mechanism of atmospheric transport to the ground is through turbulent eddies. Vertical air movement is detected at a high time resolution and air samples are taken and accumulated with each unit of up or down draft measured. Air samples associated with up and down drafts are directed to separate containers and are analysed at the conclusion of each experiment.

3.4 CONCENTRATION GRADIENT

Within the constant flux atmospheric boundary layer concentration gradients of SO_2 arise as a result of the effects of the surface sink for SO_2 acting together with the transport properties of the overlying atmosphere. The shape of the resultant concentration gradient profile reflects both of these effects.

Measurements of micrometeorological parameters such as wind speed, temperature, and water vapor concentrations allow a characterization of the turbulent transport properties within the constant flux layer. Using the so-called K-theory for turbulent transport of atmospheric constituents (see Section 2) the flux of SO_2 can be calculated from its concentration gradient and micrometeorological measurements. These measurements allow a separation to be made between the aerodynamic and surface transfer resistances for SO_2.

Concentration profile measurement techniques, although used extensively in agricultural and forestry studies of energy budgets for a number of years (Waggoner et al. 1965 , Fritschen 1970), have only been recently applied to pollution deposition studies. The dry deposition of SO_2 has been measured with this technique by Whelpdale and Shaw (1974), Shepherd (1974), and Garland (1977).

3.5 ATMOSPHERIC BUDGETS

Atmospheric budgets can be derived for SO_2 over large areas extending for hundreds of kilometers. In this "box-budget" approach SO_2 entering and leaving the area in the atmosphere is determined by vertical concentration profiles combined with wind speed measurements. A mass flux of SO_2 is found usually by a combination of ground and aircraft measurements. Area emissions of SO_2 are also added to the budget. Since the budget is calculated over periods of about 8 to 10 hours, it is necessary to include estimates of SO_2 loss by oxidation. Dry deposition for the area is found by the difference between sulfur inflow and outflow required to balance the budget. In some cases it may be necessary to include both natural and anthropogenic sources of sulfur.

Dry deposition rates inferred from measurements on this scale are usually related to long-range transport studies and transboundary flow of pollutants, (e.g. Smith and Jeffrey, 1975; Garland, 1977). The method requires large quantities of data to be collected over short periods of time. An average deposition velocity can be calculated which represents the entire area of interest over the time span of the measurements.

3.6 WATERSHED BUDGETS

Watershed studies have been carried out within which changes in sulfur content are related to the difference between total inflows and outflows of sulfur (e.g. Eaton and Likens, 1978).

Areas of tens of kilometers are studied. Waterflow rates and sulfur concentrations are determined as well as total watershed sulfur content. Changes in these values are related to a measured wet deposition of sulfur to the area and SO_2 dry deposition. Dry deposition values result from differences between relatively large numbers and are therefore of limited accuracy.

Implicit in the calculation is the assumption that all sulfur dry deposited to land surfaces within the watershed is washed into the water courses following precipitation events. The results obtained are averages over the entire watershed and during the time span of the measurements (usually several weeks).

3.7 CONTAINER EXPERIMENTS

Isolated containers of bare soil or vegetation can be inserted into the ground to blend as closely as possible with the natural background of the area. Changes in sulfur content can then be related to dry deposition if the effects of wet deposition and runoff are allowed for. Studies of this type (often referred to as lysimeter methods) have been reported by den Hartog and King (1975), Dick and Walker (1975), Shipley (1975), and Nyborg et al. (1975).

Sulfur content of the soil and vegetation are determined before and after the exposure period (usually several weeks). The change in observed sulfur content is then related to the difference between water runoff (which is monitored) and the sum of wet and dry SO_2 deposition. Wet deposition of sulfur can be monitored or prevented by an artificial cover to shield the test plot from rainfall. The result is a total dry deposition of sulfur over the experimental period. As is the case for all other mass balance approaches, this number is calculated from a difference between relatively large numbers.

3.8 TRACERS

Tracer methods can be used to measure the dry deposition of SO_2 based on the use of isotopes of sulfur released for brief periods upwind of the surface of interest. The amounts deposited on the soil and vegetation from the test release as distinguished from the naturally occurring background concentrations give a means of evaluating the dry deposition directly.

One applicaton of the method is to use radioactive ^{35}S as the tracer. Amounts in the order of 20-30 mCi are released over a test area from which samples of vegetation and soil are extracted for analysis. Simultaneous measurements of air concentrations may also be made to evaluate flux values to the ground. The collected samples then have the sulfur extracted for analysis to determine the radioactive sulfur content.

An alternative to radioactive ^{35}S as a tracer is to use the ratio of stable isotopes $^{34}S/^{32}S$ present in the release SO_2 as a self-tracer. The release material must have a $^{34}S/^{32}S$ ratio significantly different from that already present in the test site. Changes in the relative concentration of $^{34}S/^{32}S$ in the test plot are interpreted to be a result of the flux of SO_2 to the test plot from the test release.

Isotopic ratios are usually expressed as deviations from a standard in parts per thousand ($^{o}/oo$) or "dell" values. Lowe et al. (1971) has reported $\delta^{34}S$ values in Alberta values ranging from 0 to $-30^{o}/oo$, while Krouse (1977) gives typical $\delta^{34}S$ values in sulfur emitted from Alberta sour gas wells as ranging from +5 to $+30^{o}/oo$.

3.9 DEPOSITION COLLECTORS

Direct deposition collectors such as accumulation buckets, flat plates, and cylinders, etc., have been used in the past to measure bulk (total) or dry deposition (when covered during precipitation events). Although there are some dissenting opinions, the general concensus is that these methods are totally unsuitable for the determination of SO_2 dry deposition. The artificial collecting surfaces do not adequately simulate in any predictable manner the natural surfaces of interest. Furthermore, these collectors frequently disturb the aerodynamic flow such that the atmospheric transfer resistance is altered near the collector and is different than that for the natural surface under study.

The use of these types of collectors is often justified on the basis of the lack of better methods and their relatively small cost and effort. It appears that "calibration" of these surrogate surfaces may not be possible and hence data bases generated by these methods may never be useful in quantifying SO_2 dry deposition rates.

3.10 COMPARATIVE EVALUATION

The methods described above were reviewed and compared according to eight criteria. The results are summarized in Table 1 and are briefly discussed below.

3.10.1 Time Scales

The time scale over which measurements can be carried out varies considerably. Atmospheric flux methods yield results over periods of as short as a few minutes up to a few hours. Mass balance methods are applicable over periods of days to weeks as are surface accumulation techniques.

3.10.2 Space Scales

With two exceptions all of the methods considered result in data which are applicable only at the point of measurement. Atmospheric budget studies, however, apply over distances of hundreds of kilometers and watershed studies apply over distances of several kilometers.

Table 1. Suitability of various experimental methods to measure and parameterize the dry deposition rate of SO_2.

CATEGORY	METHOD	EVALUATION CRITERIA								OVERALL SUITABILITY FOR PARAMETIZATION EXPERIMENTS
		MEASUREMENT TIME SCALE	MEASUREMENT SPACE SCALE	SUITABILITY OF RESULTS TO DERIVE SO_2 FLUX	TECHNICAL DIFFICULTY	RESEARCH DEVELOPMENT REQUIRED	METHOD CURRENTLY UNDER ACTIVE CANADIAN RESEARCH	POTENTIAL ACCURACY	RELATIVE COST	
ATMOSPHERIC FLUX MEASUREMENTS	Eddy Correlation	Hours	Point	High	High	High	Yes	High	High	Medium
	Variance	Hours	Point	High	High	High	No	High	High	Medium
	Eddy Accumulation	Hours	Point	High	High	Medium	No*	High	High	High
	Concentration Gradient	Hours	Point	High	High	Medium	No	Medium	Medium	High
MASS BALANCE	Atmospheric Budget	Days	Hundreds to Thousands of Square km	Low	Very High	Low	Yes	Low	High	Very Low
	Watershed Budget	Weeks	Tens to Hundreds of Square km	Low	Medium	Low	Yes	Low	High	Very Low
	Container (Lysimeter)	Weeks	Point	Medium	Low	Low	No	Low	Low	Very Low
SURFACE ACCUMULATION	^{35}S	Days	Tens to Hundreds of Square Metres	High	Medium	Low	No	High	Medium	Very Low
	$^{34}S/^{32}S$	Days to Weeks	Tens to Hundreds of Square Metres	High	Medium	Low	No	Medium	Medium	Very Low
	Deposition Collector	Weeks	Point	Very Low	Low	High	No	Very Low	Very Low	Very Low

*This method is currently under active research development for some parameters other than SO_2

3.10.3 Suitability of Results

The applicability of the results of the various methods in deriving meaningful SO_2 deposition rates from the experimental data is variable. Atmospheric flux measurements are easily translated into deposition rates (provided the site and meteorological criteria are met). Tracer studies, ^{35}S and $^{34}S/^{32}S$, also provide results which are reliably representative of SO_2 deposition rates. Small container experiments are good for providing dry deposition rates of SO_2 provided other processes such as wet deposition and sulfur leaching are adequately assessed. Atmospheric budget and watershed study data are more difficult to interpret, however, due to uncertain assumptions required in the data analysis. The use of surrogate surfaces for deposition collection yields data which are extremely difficult to interpret.

3.10.4 Technical Difficulty

Atmospheric flux measurements all present a fair degree of technical difficulty to carry out. These are not suitable for routine unskilled application. Tracer studies are somewhat easier to carry out while watershed, container studies, and deposition collector techniques are easily applied. Atmospheric budget studies present very difficult technical problems which need to be overcome to obtain useful results.

3.10.5 Research Development Required

Instrumental packages for atmospheric flux techniques suitable for SO_2 deposition studies are not generally available commercially. Some components (e.g. suitable SO_2 analysers) are currently only at the prototype stage and hence application of these methods must still be considered as a research and development program. Deposition collectors require further research if their results are to be related to SO_2 deposition to natural surfaces. The investment of research effort into this method is, however, of questionable value. The other techniques considered do not require additional research or development.

3.10.6 Current Active Canadian Research

Several of the methods discussed have been used in Canada to determine SO_2 deposition rates. However, at the present time research efforts are active on only the eddy correlation, atmospheric budget, and watershed budget techniques.

Both the Federal Government (Environment Canada) and Ontario Hydro are developing eddy correlation methods. Environment Canada plans to use a fast response flame photometric detector, while Ontario Hydro has just initiated the development of a diode laser detection system as a chemical sensor. It is not expected that either study will produce results this year.

The eddy accumulation method has been the subject of considerable research and development by Agriculture Canada (Desjardins, 1980). The method has been applied to CO_2 and water vapor, but not SO_2. Further development is needed to apply the method to trace pollutants such as SO_2.

3.10.7 Potential Accuracy

The potential accuracy of the methods assessed is satisfactory with the exception of the atmospheric and watershed budget techniques and the deposition collector method.

3.10.8 Relative Costs

Most of the techniques reviewed are either moderately or highly expensive with the exception of the container (lysimeter) and the deposition collector methods which are relatively low cost experiments.

3.10.9 Overall Suitability for Parameterization Experiments

The parameters which influence SO_2 deposition rate can frequently vary over time scales of hours and therefore any experimental program chosen to establish a relationship betwen deposition rates and these parameters must be capable of making measurements over similar time periods. On this basis alone, all of the mass balance and surface accumulation methods are not suitable.

All four atmospheric flux techniques are suitable for parameterization experiments. However, the eddy correlation and variance methods present the most difficult requirements for the chemical sensor (fast time response and high sensitivity). The eddy correlation approach is currently being developed by both Environment Canada and Ontario Hydro. For these reasons, the eddy accumulation and concentration profile methods were evaluated as being the most suitable for parameterization experiments to be carried out in phase two of this study.

4. CHEMICAL SENSOR FOR SO_2

Both the concentration profile and eddy accumulation methods require an SO_2 sensor of high precision and sensitivity. Since both rely on measurements of concentration differences rather than absolute concentrations then a continuous monitor should be more suitable than discrete sampling and analytical methods. It is anticipated that concentration differences of less than 5 % will be required to be measured. Hence a precision of better than 1 % is required. This must be achievable for SO_2 concentrations of 10 ppb and lower.

There are no commercially available SO_2 monitors which meet these specificaions. The closest is the Meloy Laboratories Inc. flame photometric SO_2 monitor. This monitor uses the so-called flame photometric detection (FPD) method - basically sulfur compounds are detected by emissions of light when they pass through a hydrogen rich flame. In the flame region, electronically excited S_2 molecules are formed. These emit light during relaxation to the ground state over a broad band centered at about 394 nm. These light emissions are detected by a photomultiplier tube (PMT) which produces a signal related to the amount of sulfur present. The PMT signal, I_s, depends in theory on the square of the amount of sulfur present.

$$I_s = KC^m \tag{12}$$

Here K is a constant, C is the sulfur concentration, and m is a constant theoretically equal to two. In practice m is found to vary from 1.5 to 2.0 (D'Ottavio et al. 1981).

This response characteristic implies an increase in sensitivity with increasing sulfur concentration.

$$\frac{dI_s}{dc} = mKc^{m-1} \tag{13}$$

The derivative of I_s by C expresses the response sensitivity as a function of concentration. This offers the possibility of enhanced sensitivity operation by sulfur addition to the sample stream. Sensitivity enhancement has been achieved by the use of SO_2 added to the H_2 stream (Crider et al. 1969 , Zehner et al. 1976). However, better results have been recently reported by D'Ottavio et al. (1981) using SF_6 mixed with the H_2 stream. Hence sensitivity enhanced FPD was selected as the most promising method for SO_2 monitoring.

A Meloy SA260 sulfur analyser was used with a fast time response option and without log-linear signal processing. In place of the usual H_2 carrier gas a mixture of SF_6/H_2 was used with an SF_6 concentration of about 100 ppb. Calibration of the system was carried out using a flow proportioner to mix zero air streams and SO_2/N_2 mixtures. Concentrations to below 1 ppb were relatively easily produced.

Typical calibration curves are shown on Figure 1 and Figure 2 (0-180 ppb and 0-3.4 ppb). The non-linear response is apparent even over the range of 0-3.4 ppb. Based on a signal to noise ratio of two the estimated limit of detection is 0.04 ppb. This represents an improvement of a factor of 25 over that obtainable under normal operation. Other characteristics such as zero drift and calibration changes have not been fully evaluated as yet, however, indications are that operation of the monitor is fairly stable over periods of hours.

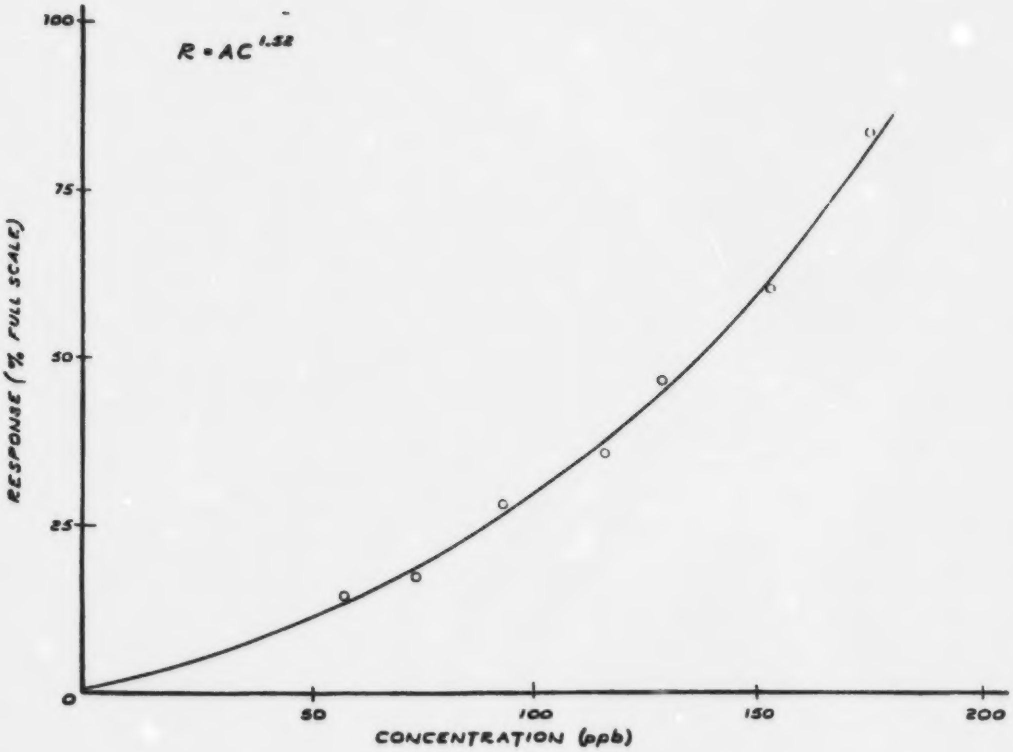


Figure 1. Meloy SA 260 sulfur analyzer with sensitivity enhancement - Calibration 0-180 ppb.

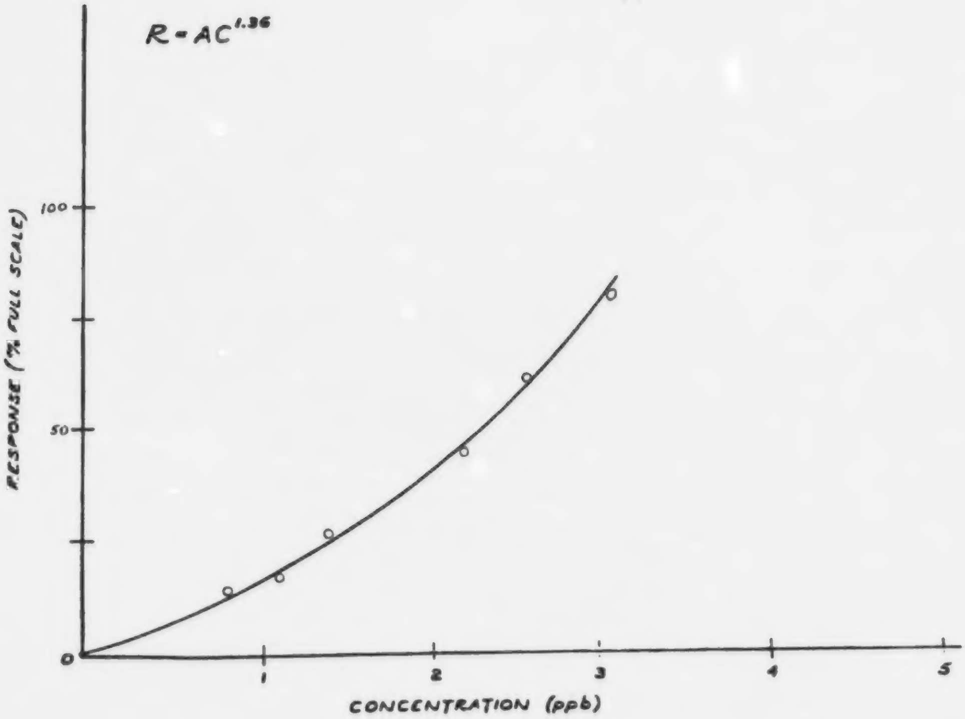


Figure 2. Meloy SA 260 sulfur analyzer with sensitivity enhancement - Calibration 0-3.4 ppb.

5. CONCENTRATION GRADIENT PROFILE SYSTEM

A sampling system has been constructed to allow SO_2 concentration profiles to be determined using the Meloy SO_2 monitor (see Figure 3). Three sample lines, 3/16" teflon, of equal length are connected through 1 liter mixing chambers to a common 5 liter ballast volume. This connects to a vacuum pump which draws a sampling volume of about 1 liter per minute from each line. The sampling lines are heat traced to avoid possible condensation. Samples for analysis are drawn through a four-way valve between the mixing chambers and ballast volume. The position of this valve determines which sample line is analyzed. Between this valve and the analyzer are a particulate matter filter (teflon) and an H_2S scrubber.

Calibration mixtures and zero air are connected between the four-way valve and the particulate filter for frequent calibration and zero drift checks. The system response time to 99 % of signal was found to be less than about 20 seconds. This allows all three lines to be analyzed within about a 1 minute period which corresponds to the residence time of samples in each mixing chamber.

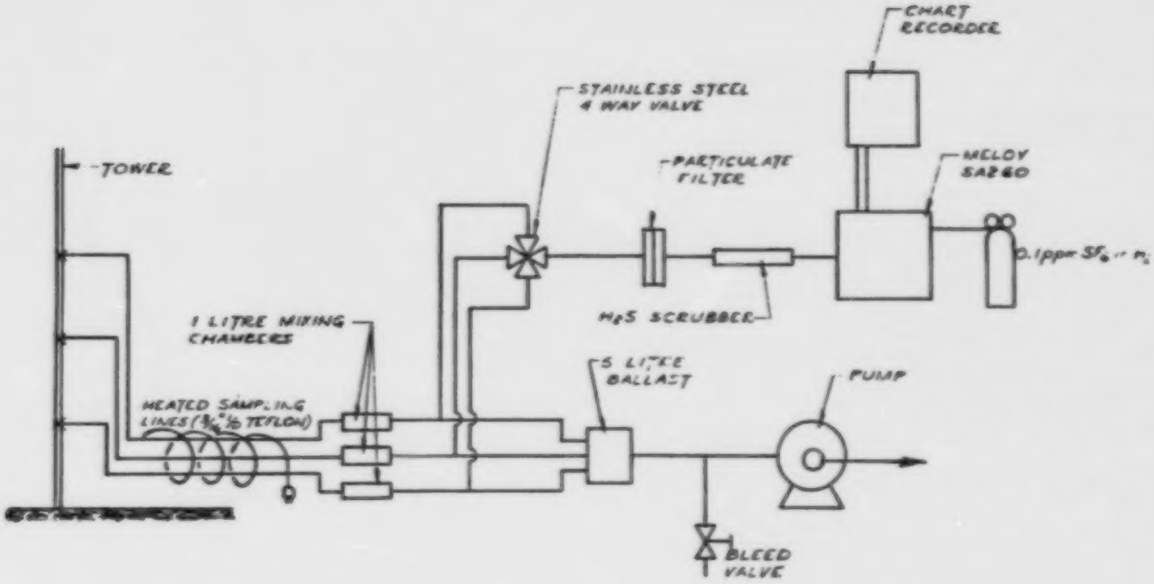


CHART RECORDER
STAINLESS STEEL 4 WAY VALVE
PARTICULATE FILTER
MELOY SA260
TOWER
0.1ppm SF_6 in N_2
H_2S SCRUBBER
1 LITRE MIXING CHAMBERS
5 LITRE BALLAST
PUMP
HEATED SAMPLING LINES (3/16" 1/8 TEFLON)
BLEED VALVE

Figure 3. Concentration gradient profile system.

6. EDDY ACCUMULATION SAMPLING SYSTEM

The eddy accumulation sampling systems is seen in Figure 4. During usual operation, samples are accumulated in plastic or teflon sample bags contained within a rigid chamber which is brought to low pressure by a vacuum pump. This provides a vacuum along the sampling lines. There are two sampling lines and accumulation containers. One corresponds to updrafts, the other to downdrafts. Sampling in each line is controlled by a small valve which opens momentarily in response to a measured preselected incremental up or downdraft as measured by a nearby anemometer.

Since laboratory tests failed to identify a container able to hold the collected SO_2 without loss prior to analysis, the sampling system was modified for the preliminary field tests. The sample bags were bypassed and instead samples were taken, without accumulation, directly to the analyzer. Between sample pulses zero air was admitted to the top of the sampling line in order to maintain a continuous flow of sample to the analyzer. In this configuration, the analyzer was set to sequentially monitor updrafts and downdrafts for periods of several minutes each.

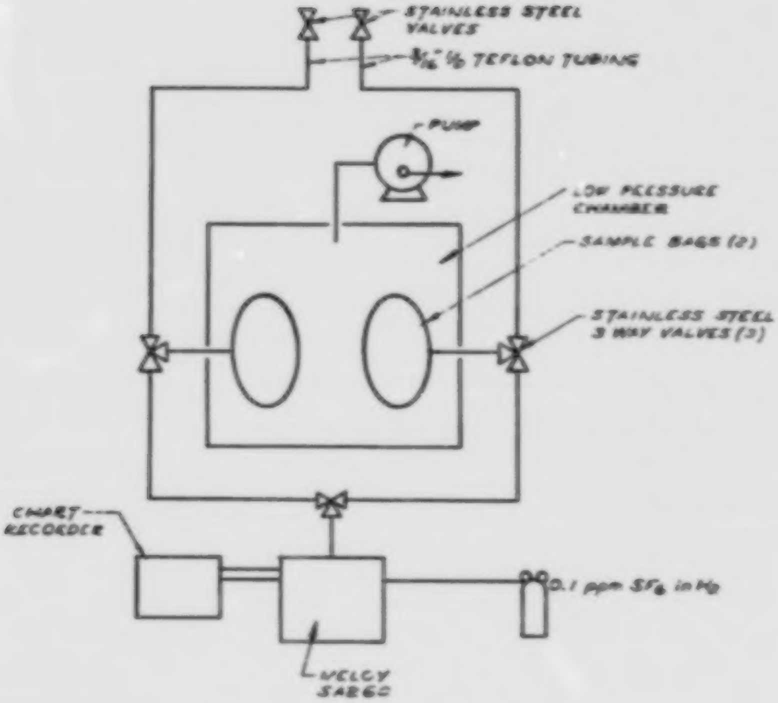

STAINLESS STEEL VALVES
3/16" I/D TEFLON TUBING
PUMP
LOW PRESSURE CHAMBER
SAMPLE BAGS (2)
STAINLESS STEEL 3 WAY VALVES (3)
CHART RECORDER
0.1 ppm SF6 in N2
WELCY SA86C

Figure 4. Eddy accumulation system.

7. PRELIMINARY FIELD STUDY RESULTS

Both concentration profile and eddy accumulation experiments were carried out during a preliminary field study in Ottawa at a test site used by the federal Department of Agriculture. The site is ideal for micrometeorological studies and consists of a large, uniform, flat field of about 60 acres (1000 feet square). There was a stand of alfalfa in the field but it was dead at the time of the study (October 17, 1981).

The day prior to the study a cold front passed by the area leaving the field wet during the period of measurements. There was a northerly flow into the area and prevailing SO_2 concentrations were quite low at from 1.0 to 1.5 ppb.

7.1 EDDY ACCUMULATION RESULTS

The modified sampling system was used as described in Section 6. Since it was necessary to add zero air to the sample lines the sample concentrations were consequently diluted. The extent of dilution depends on the sample pulse size, and the frequency at which sample pulses are taken. This frequency is determined by the turbulence intensity of the atmosphere during the experimental period. For this study a dilution of about a factor of twenty was experienced. This resulted in SO_2 concentrations of only about 0.05 ppb. At these low levels it was not possible to measure concentration differences between up and downdraft samples.

7.2 CONCENTRATION GRADIENT PROFILE RESULTS

As discussed in Section 3, concentration gradient methods require a number of micrometeorological measurements to be taken at the same time as the SO_2 concentrations. Existing facilities at the site provided profiles of temperature and relative humidity, net radiation and surface heat flow by heat plates at 5 cm depths.

The profile systems were set up to measure parameters up to only about 3 m from the ground and hence SO_2 concentration data were also limited to this height.

Energy balance data and, temperature and relative humidity profiles were combined to determine a value for the eddy diffusivity for sensible heat, K_H. Assuming similarity between sensible heat and SO_2 then K_{SO_2} was taken as equal to K_H. Combining K_{SO_2} and SO_2 concentration gradients gave a value for the flux of SO_2 to the surface. This flux and the observed ambient concentration of SO_2 then yield a deposition velocity.

Measurements during the day at 13:30 and 14:00 yielded values of 1.53 and 1.33 $cm \cdot sec^{-1}$ respectively. This is reasonable for a wet field during the conditions prevailing at the time. A third measurement at 16:00 gave a value of 0.16 $cm \cdot sec^{-1}$. Examination of the temperature profile data indicates that a ground based inversion was starting to form at 15:00 and was well established by 17:30. Hence the low apparent deposition velocity at 16:00 was likely due to change over conditions and the formation of an inversion layer which resulted in an increased aerodynamic resistance to SO_2 transfer.

8. CONCLUSIONS

Although there are a variety of methods available to estimate SO_2 deposition rates, the most promising techniques which would allow a parameterization of deposition velocity in terms of other more easily measured factors appears to be eddy accumulation and concentration gradient profiles. For both of these methods a very sensitive SO_2 monitor is required and it appears that FPD with enhanced sensitivity by SF_6 will prove satisfactory.

The eddy accumulation technique needs development to reduce the dilution factor of samples if it is to be useful. A new sampling valve currently being tested may overcome this problem. It appears unlikely that suitable storage containers will be found without extensive work.

The concentration gradient profile method has produced reasonable results. A larger sampling height and more sample points should be used. However, preliminary results are very encouraging.

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ACIDITY AND CHEMICAL COMPOSITION OF PRECIPITATION IN CENTRAL ALBERTA, 1977-1978

R.F. KLEMM[1], J.M.L. GRAY[1]

Abstract

Precipitation events occurring during the summers of 1977 and 1978 and within a 30-km radius of Edmonton were studied using a 60-site sampling network. Total catch from such events were analyzed for pH, conductivity, and 22 ionic species. Median pH's for individual rains ranged from 4.4 to 5.8. Extensive statistical analyses of the data suggest that the ions $SO_4^=$, NO_3^-, NH_4^+, and Ca^{++} can explain no more than 70% of the variation in acidity.

For the major ions, the median concentration (mg/L) derived from all precipitation events sampled are as follows: Na^+ (0.06), NH_4^+ (0.41), K^+ (0.09), Ca^{++} (0.60), Mg^{++} (0.05), Cl^- (0.10), NO_3^- (0.72), $SO_4^=$ (1.52). A mean pH = 5.3 is also indicated. Satisfactory ionic charge balances could be achieved in the case of individual storms using the above species and a calculated bicarbonate ion concentration. All other chemical species measured were at the µg/L level and did not affect the charge balance.

During some occurences, sequential as well as bulk samples were taken. Based upon such sequential samples, the variation in chemical species concentration during the course of individual events will be examined in detail.

Also during 1977 and 1978, a second "dense" network of sampling sites was used to detail, as above, the chemical composition of rain occurring in the area from west of Rocky Mountain House to east of Red Deer. Again, both total catch and sequential sampling were carried out. Results from this frequently studied area will be compared both with previous data from the area and with the Edmonton results as summarized above.

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1. INTRODUCTION

Although the Canadian precipitation sampling network (CANSAP) operates five stations in Alberta, and Alberta Environment recently began monitoring the chemical characteristics of rain and snow in the province on a monthly basis, to date no detailed chemical analyses of individual storms have been attempted for the Edmonton, Rocky Mountain House (RMH), or Red Deer (RD) areas. This paper presents measurements of 22 chemical species in bulk samples from "typical" events showing the salient findings from sampling individual storms during 1977 and 1978. Some sequential sampling results are also presented. Information accumulated from this work has been used to compare the frequency and chemical constituents of "acid rain" in the RD-RMH area with the Edmonton metropolitan area.

2. EXPERIMENTAL

The bulk samples were obtained from 2 mil polyethylene bags secured to 25 cm diameter frames approximately 1.5 m above ground level. These were set out before an event and retrieved after its termination. Sequential samples were generally obtained from an equal volume partitioning device; although occasionally, time sequenced samples were also taken. The samples were filtered, the pH and conductivity were measured, and the samples were then frozen (-17 C) for later analysis.

Chloride, nitrate, sulphate, ammonium, sodium, and potassium were analyzed by ion chromatography. The other species were analyzed by atomic absorption spectroscopy.

3. RESULTS

Samples were collected from twenty storms in the Edmonton and RD-RMH areas. Snow samples were also collected in the RD-RMH area. More than 4 000 analytical determinations were obtained from these samples. Representative data have been selected to illustrate the generally observed interspecies relationships and differences between chemical concentrations in Edmonton and RD-RMH precipitation.

3.1 EDMONTON: 10 MAY 1978

Figure 1 (see 5. Appendix:Figures) is a pseudo three-dimensional computer plot of the geographical distribution of pH as measured for the storm of 10 May. Acidic rain was found at all sites south of Edmonton city centre. Surface winds recorded at Edmonton Municipal and at Edmonton International airports were available from southwest clockwise to northeast, averaging km/h, so that rains collected everywhere south of the city probably had originated in air masses which had passed over the Edmonton metropolitan area. A study of Figures 2 to 5, suggests that, in this instance the acid rain was related to reduced buffering by the low concentrations of calcium species, rather, than the presence of large amounts of acidic nitrate and sulphate species. The traces of rain recorded on 8 and 9 May apparently did not affect the concentration of suspended airborne surficial material since significant amounts of these species are present in the precipitation (Tables 1 and 2).

The high correlation between sulphate and nitrate in Table 1 becomes more apparent upon comparison of Figures 4 and 5. Both species tend to occur in higher concentrations in an arc north of Edmonton centre. These relatively high concentrations of sulphate and nitrate were not associated with lowered pH values because the acidic component was neutralized sufficiently by correspondingly elevated concentrations of basic calcium and ammonium species. The low pH values generally were a consequence of insufficient basic calcium and ammonium compounds to neutralize the acidic nitrate and sulphate species.

3.2 RED DEER-ROCKY MOUNTAIN HOUSE: 16 JULY 1978

Surface winds were study from WNW on this date. Figures 6 to 10 illustrate typical distributions of the chemical species found in the RD-RMH area. The acidic pH's observed to the extreme south of RMH in Figure 6 occurred in the immediate vicinity of two large sour gas processing plants. These acidic pH's were associated with elevated sulphate concentrations, average nitrate concentrations, and low calcium and ammonium concentrations. A tendency toward generally higher sulphate concentrations in the southern half of the measurement area was also observed (Figure 10).

Table 1. Significant species correlations: Edmonton - 10 May 1978

Species	Correlation Coefficient
Ca - Si	0.95
Ca - Cr	0.93
Al - Si	0.93
Ca - Mg	0.84
Cr - Al	0.91
Si - Cr	0.99
NO_3^- -$SO_4^=$	0.92

Table 2. Species concentrations (mg/L): Edmonton - 10 May 1978

Species	Average	S.D.	Median	Maximum	Minimum
pH	5.6	0.8	5.6	7.3	4.6
$SO_4^=$	2.9	1.4	2.8	5.8	0.6
NO_3^-	1.2	0.5	1.1	2.4	0.3
NH_4^+	0.7	0.4	0.7	1.9	0.06
Ca	1.0	1.4	0.6	9.1	0.2

Figure 7 shows the low concentrations of ammonium found west of RMH and the trend toward higher values as one proceeds eastward into more populated agricultural areas. However, without a concentrated season-long monitoring program, it is difficult to determine if this particular distribution of ammonium values was related to fertilizing practices.

Interspecies correlation coefficients greater than 0.8 for 16 July 1978 are presented in Table 3. The high positive correlation between pH and calcium for this storm confirms the more general observation recorded in almost every event studied: the pH of the precipitation is more strongly dependant upon the presence or absence of buffering agents than upon acidic nitrate and sulphate species.

Table 4 summarizes the important species concentrations for 16 July 1978. Additional details concerning the relationships between various species can be determined by sequentially sampling individual storms. Some sequential data for a thunderstorm on 17 July 1978 are shown in Figure 11. Interesting factors are: (1) the progressive decrease of calcium (and by inference other suspended particulate), (2) the essentially constant concentrations of sulphate, nitrate, chloride, ammonium, potassium, sodium, and magnesium, and (3) the abrupt decrease in pH during the storm paralleled by the increase in nitrate which was probably generated by storm activity. The pH at any time combination of chemical and physical parameters which may not be evident from bulk sample data alone.

3.3 RED DEER-ROCKY MOUNTAIN HOUSE TOTAL DEPTH OF SNOW

The simplest means of evaluating the integrated seasonal winter deposition involves analyses of total depth of snow. While this causes some problems in assessing total concentrations of water soluble species because of thaw-freeze cycles, some general conclusions can still be derived. Our data for snow samples on 24 to 28 January 1978 are summarized in Figures 12 to 16 and Table 5.

The average and median pH's suggest that an acidic spring run-off would not be an extensive problem over most of the area. Of the 63 measurement sites, pH values less than 5.1 were recorded at only nine sites. These low values were observed in the south and east half

Table 3. Significant species correlationS RD-RMH: 16 July 1978

Species	Correlation Coefficient	Species	Correlation Coefficient
pH - Ca	0.83	K - Si	0.85
$Na^+ - NH_4^+$	0.83	Ca - Si	0.80
$Na^+ - Cl^-$	0.98	Cl - Fe	0.85
$NH_4^+ - Cl^-$	0.81	Fe - Al	0.90

Table 4. Species concentrations (mg/L) and pH, Red Deer-Rocky Mountain House: 16 July 1978.

Species	Average	Maximum	Minimum	Median	S.D.
pH	5.4	7.2	4.3	4.9	1.0
$SO_4^=$	1.7	3.5	0.9	1.6	0.6
NO_3^-	0.6	1.7	0.1	0.5	0.3
NH_4^+	0.3	2.5	0.01	0.2	0.3
Ca	1.1	4.6	0.2	0.7	1.1

Table 5. Species concentrations (mg/L) and pH for total depth of snow: RD-RMH 1978/79.

Species	Average	Maximum	Minimum	Median	S.D.
PH	5.8	8.4	4.6	5.7	0.7
$SO_4^=$	0.9	2.1	0.5	0.8	0.3
NO_3^-	0.9	0.5	0.5	0.9	0.3
NH_4^+	0.2	0.6	0.01	0.2	0.1
Ca	0.8	13.9	0.1	0.5	1.7

of the measurement area (Figure 12). Two sites in close proximity to the two large sour gas processing plants south of RMH showed low pH values, similar to values determined for the rain samples.

The uniformly low concentration of ammonium in the snow of the foothills region south and west of RMD is similar to the spatial distribution seen in summer storms (compare Figures 7 and 13). Although not as pronounced, the distribution patterns of the remaining species are also similar to those noted for the summer storms. The results are in accord with the proposition that acidity in the area is more often controlled by buffering species than by sources of strong acids, except in the immediate vicinity of sour gas processing plants.

Using the concentration data of Figures 12 to 16, we calculate a maximum sulphate deposition of 0.5 kg/ha and an average sulphate deposition of 0.2 kg/ha.

The nitrate deposition increased gradually but definitely from 0.2 kg/ha west of RMH to 0.5 kg/ha at the eastern limit of the sampling network.

4. SUMMARY AND CONCLUSIONS

Median values by study area for all species measured are compiled in Table 6. Except for calcium and sulphate and some of the heavy metals, all other species occur in higher concentrations in the Edmonton precipitation. The pH distributions for Edmonton and RD-RMH are shown in Figure 17. The pH distributions are essentially identical as are the median values. Less than 20% of the pH values were below pH 5 and none were below pH 4. These results are in marked contrast to data for eastern North America and Western Europe where the distribution curves rise more steeply and are shifted to median pH's of 4.5 to 4.3. The Alberta rains are thus about 10 times less acid.

The sulphate and nitrate concentrations are generally large enough to indicate that acid rain would be produced if at least part of the potential acidity was not neutralized. The pH determining species for both rain and snow samples are therefore basic species containing calcium and ammonium rather than acidic nitrate and sulphate species.

Table 6. Summary of Species Measured

Species	Edm.Rain	RD Rain	RD T.Snow	Species	Edm.Rain	RD Rain	RD T.Snow
pH	5.3	5.4	5.7	Fe	4.9	1.0	6.0
Na^+	0.07	0.02	0.05	Al	7.4	2.0	11.0
K^+	0.10	0.02	0.04	Si	40.0	6.6	18.5
NH_4^+	0.44	0.13	0.21	Pb	1.0	0.9	1.0
Ca	0.16	0.19	0.25	Zn	4.0	1.1	1.4
Mg	0.06	0.06	0.05	Cu	0.5	0.3	0.3
Cl^-	0.12	0.05	0.12	Ni	1.0	1.0	1.0
$SO_4^=$	1.34	1.12	0.83	Cd	<0.5	<0.5	<0.5
$H_2PO_4^-$	<0.5	<0.5	<0.5	Cr	<0.5	<0.5	<0.5
				Mn	4.4	2.8	5.4
				Co	<0.5	<0.5	<0.5

5. APPENDIX: FIGURES

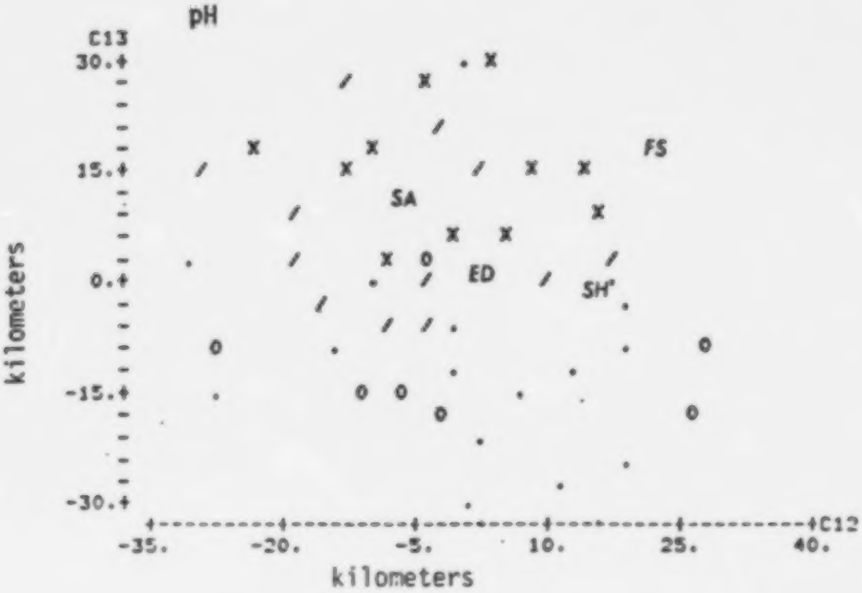
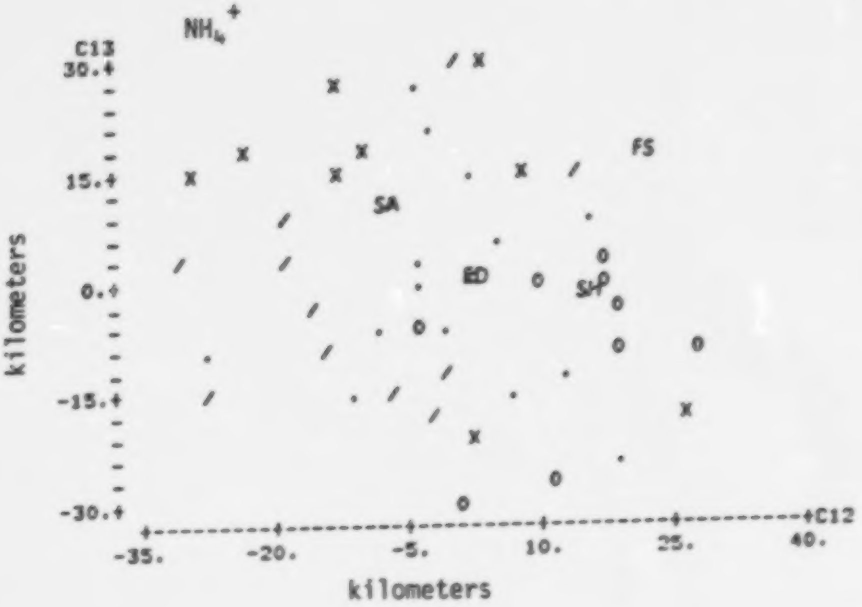


Figure 1. Geographical distribution of pH. Edmonton 10 May 1978.

O DENOTES VALUES L.T. 4.79657
. DENOTES VALUES L.T. 5.63630
/ DENOTES VALUES L.T. 6.47603
X DENOTES VALUES G.T. 6.47603

ED - EDMONTON
FS - FORT SASKATCHEWAN
SA - SAINT ALBERT
SH - SHERWOOD PARK



NH_4^+
C13
30.
15.
0.
-15.
-30.
kilometers
SA
ED
FS
SH
-35.
-20.
-5.
10.
25.
40.
C12
kilometers

Figure 2. Geographical distribution of NH_4^+ concentrations (mg/L). Edmonton. 10 May 1978.

O	DENOTES VALUES L.T.	0.29069	ED - EDMONTON
.	DENOTES VALUES L.T.	0.74953	FS - FORT SASKATCHEWAN
/	DENOTES VALUES L.T.	1.20838	SA - SAINT ALBERT
X	DENOTES VALUES G.T.	1.20838	SH - SHERWOOD PARK

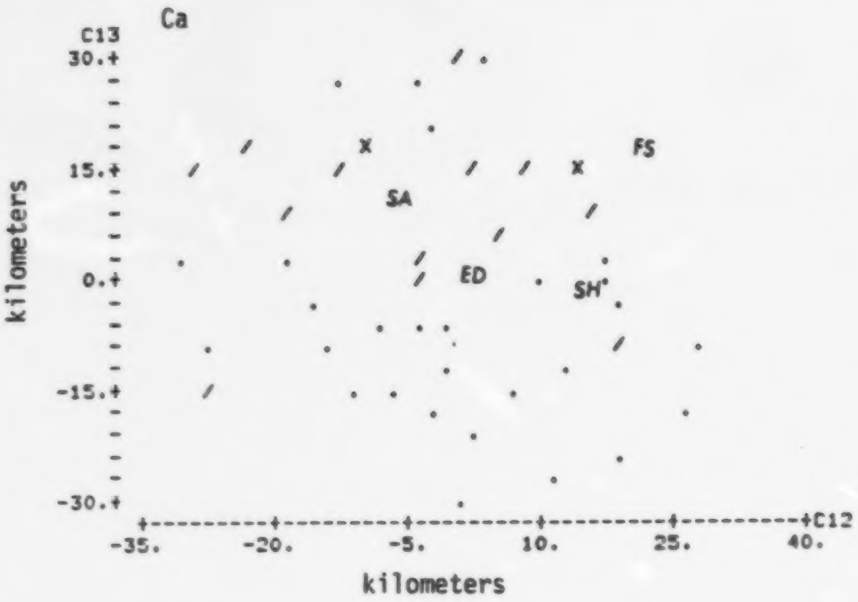

Ca
C13
30.
15.
0.
-15.
-30.
kilometers
SA
ED
SH
FS
-35.
-20.
-5.
10.
25.
40.
C12
kilometers

Figure 3. Geographical distribution of Ca concentrations (mg/L).
Edmonton 10 May 1978.

O DENOTES VALUES L.T. -0.34663
. DENOTES VALUES L.T. 1.01535
/ DENOTES VALUES L.T. 2.37733
X DENOTES VALUES G.T. 2.37733

ED - EDMONTON
FS - FORT SASKATCHEWAN
SA - SAINT ALBERT
SH - SHERWOOD PARK

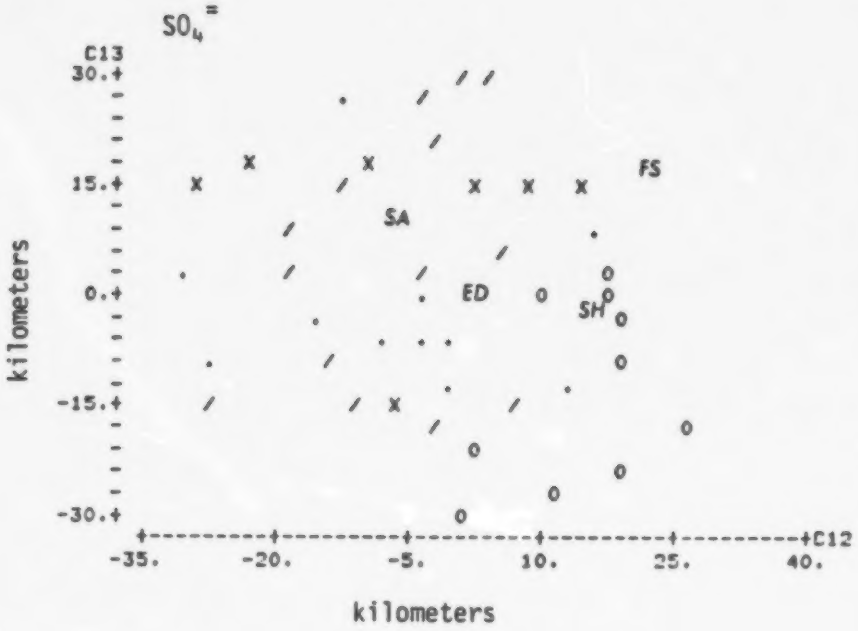

$SO_4^=$
C13
30.
15.
0.
-15.
-30.
-35.
-20.
-5.
10.
25.
40.
C12
kilometers
kilometers
FS
SA
ED
SH

Figure 4. Geographical distribution of $SO_4^=$ (mg/L) concentrations. Edmonton 10 May 1978.

O DENOTES VALUES L.T. 1.41428
. DENOTES VALUES L.T. 2.86619
/ DENOTES VALUES L.T. 4.31810
X DENOTES VALUES G.T. 4.31810

ED - EDMONTON
FS - FORT SASKATCHEWAN
SA - SAINT ALBERT
SH - SHERWOOD PARK

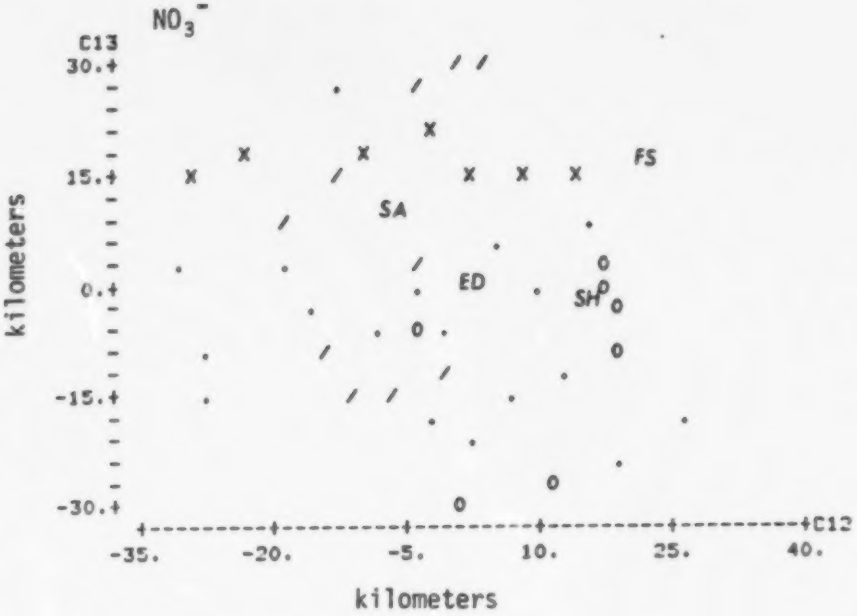

NO3-
C13
30.
15.
0.
-15.
-30.
kilometers
SA
ED
FS
SH
-35.
-20.
-5.
10.
25.
40.
C12
kilometers

Figure 5. Geographical distribution of NO_3^- compositions (mg/L). Edmonton 10 May 1978.

O DENOTES VALUES L.T. 0.67033
. DENOTES VALUES L.T. 1.20524
/ DENOTES VALUES L.T. 1.74014
X DENOTES VALUES G.T. 1.74014

ED - EDMONTON
FS - FORT SASKATCHEWAN
SA - SAINT ALBERT
SH - SHERWOOD PARK

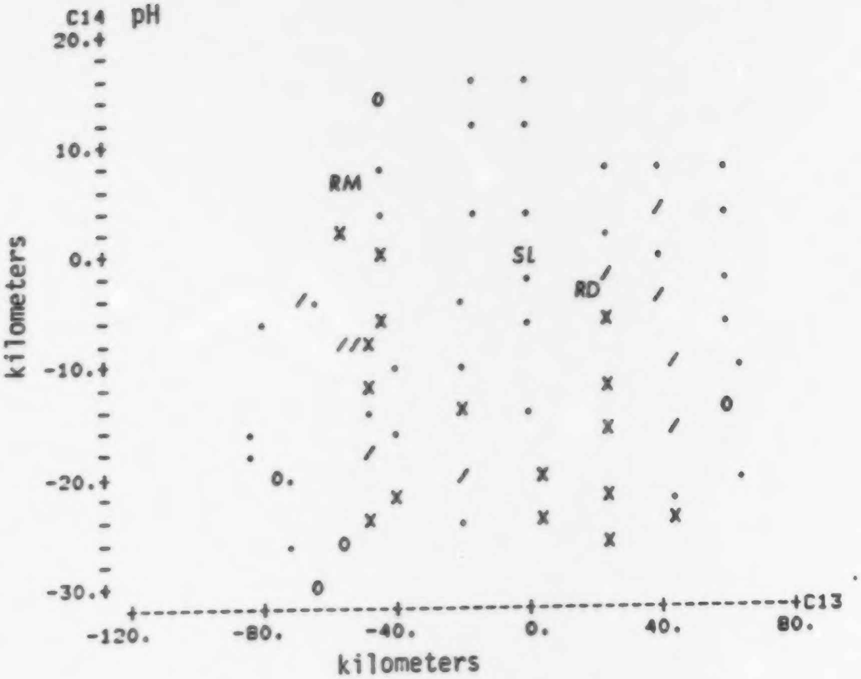


Figure 6. Geographical distribution of pH. Red Deer-Rocky Mountain House. 16 July 1978.

O DENOTES VALUES L.T. 4.44324
. DENOTES VALUES L.T. 5.38723
/ DENOTES VALUES L.T. 6.33122
X DENOTES VALUES G.T. 6.33122

RD - RED DEER
RM - ROCKY MOUNTAIN HOUSE
SL - SYLVAN LAKE

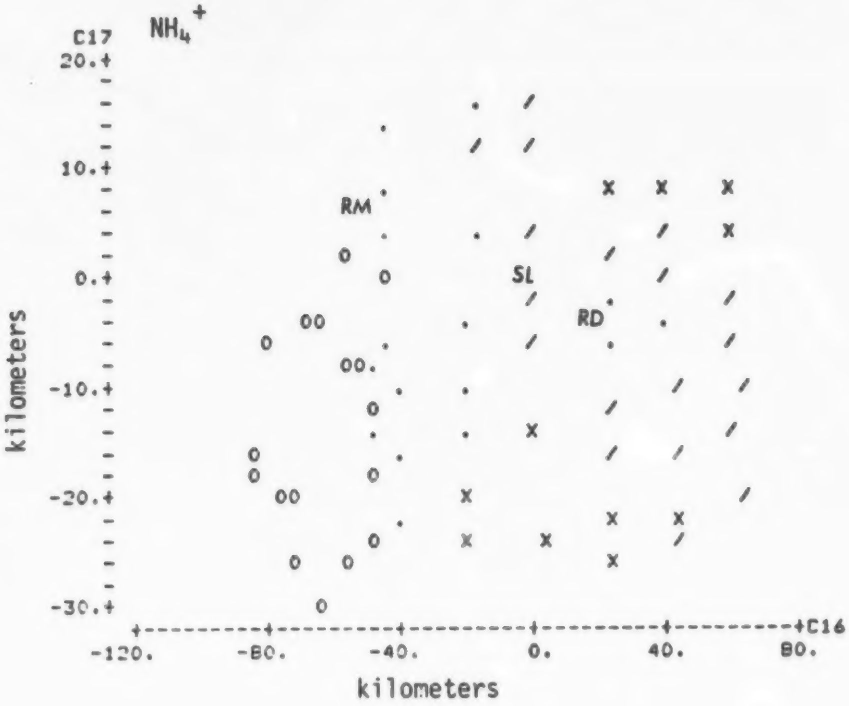


Figure 7. Spatial distribution of NH_4^+ concentrations (mg/L). Red Deer-Rocky Mountain House. 16 July 1978.

O DENOTES VALUES L.T. 0.06467
. DENOTES VALUES L.T. 0.23883
/ DENOTES VALUES L.T. 0.41299
X DENOTES VALUES G.T. 0.41299

RD - RED DEER
RM - ROCKY MOUNTAIN HOUSE
SL - SYLVAN LAKE

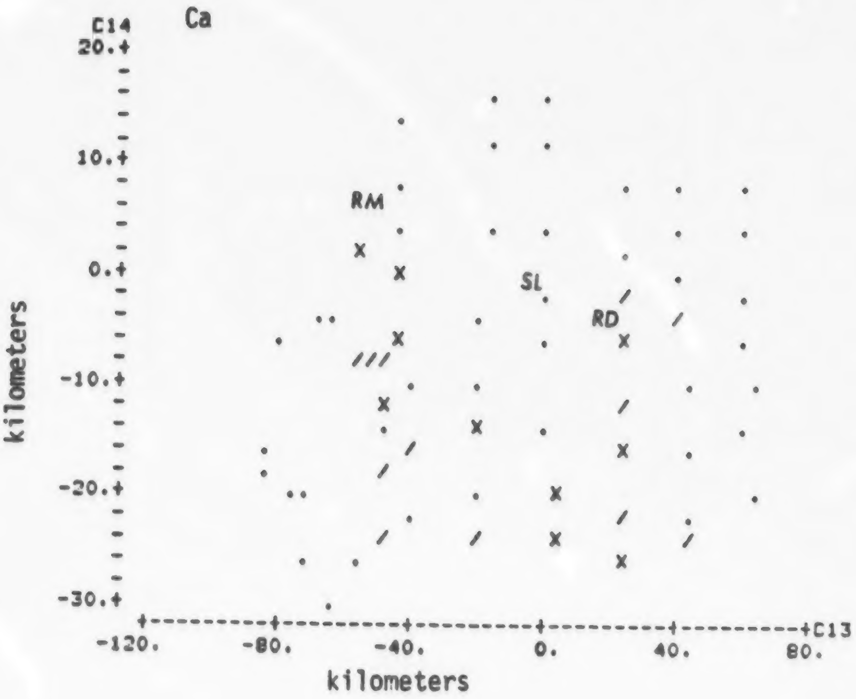


Figure 8. Spatial distribution of Ca concentrations (mg/L). Red Deer-Rocky Mountain House. 16 July 1978.

O	DENOTES VALUES L.T.	0.03731
.	DENOTES VALUES L.T.	1.10892
/	DENOTES VALUES L.T.	2.18053
X	DENOTES VALUES G.T.	2.18053

RD - RED DEER
RM - ROCKY MOUNTAIN HOUSE
SL - SYLVAN LAKE

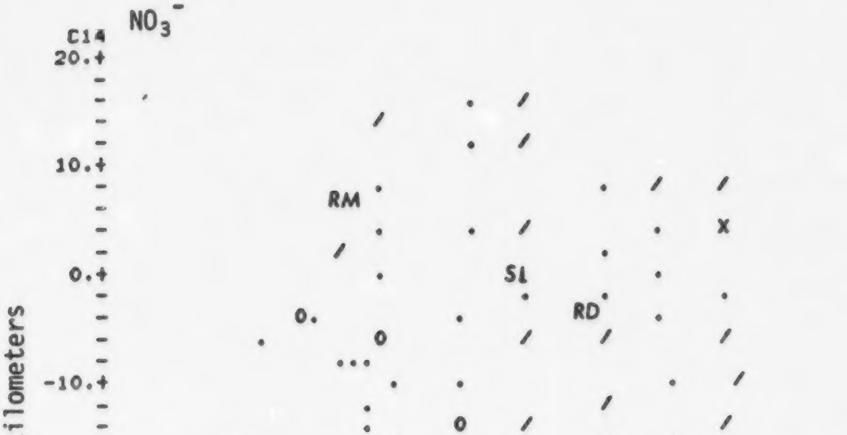

NO3-
C14
20.
10.
0.
-10.
-20.
-30.
kilometers
RM
SL
RD
C13
-120.
-80.
-40.
0.
40.
80.
kilometers

Figure 9. Geographical distribution of NO_3^- concentrations (mg/L). Red Deer-Rocky Mountain House. 16 July 1978.

O	DENOTES VALUES L.T.	0.31433	RD - RED DEER
.	DENOTES VALUES L.T.	0.59492	RM - ROCKY MOUNTAIN HOUSE
/	DENOTES VALUES L.T.	0.87552	SL - SYLVAN LAKE
X	DENOTES VALUES G.T.	0.87552	

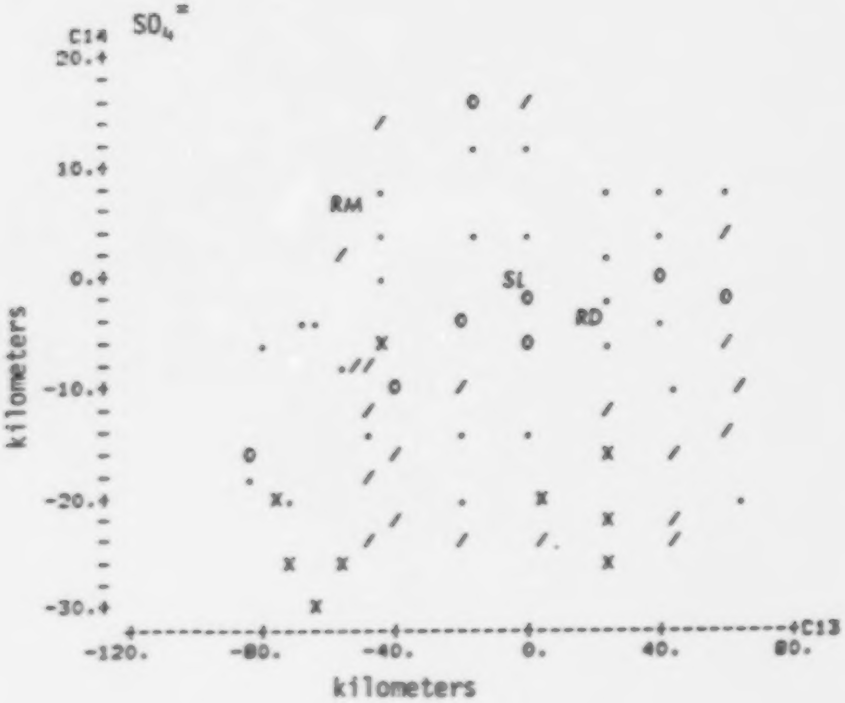


Figure 10. Geographical distribution of $SO_4^=$ concentrations (mg/L). Red Deer-Rocky Mountain House. 16 July 1978.

O DENOTES VALUES L.T. 1.10840
. DENOTES VALUES L.T. 1.68523
/ DENOTES VALUES L.T. 2.26206
X DENOTES VALUES G.T. 2.26206

RD - RED DEER
RM - ROCKY MOUNTAIN HOUSE
SL - SYLVAN LAKE

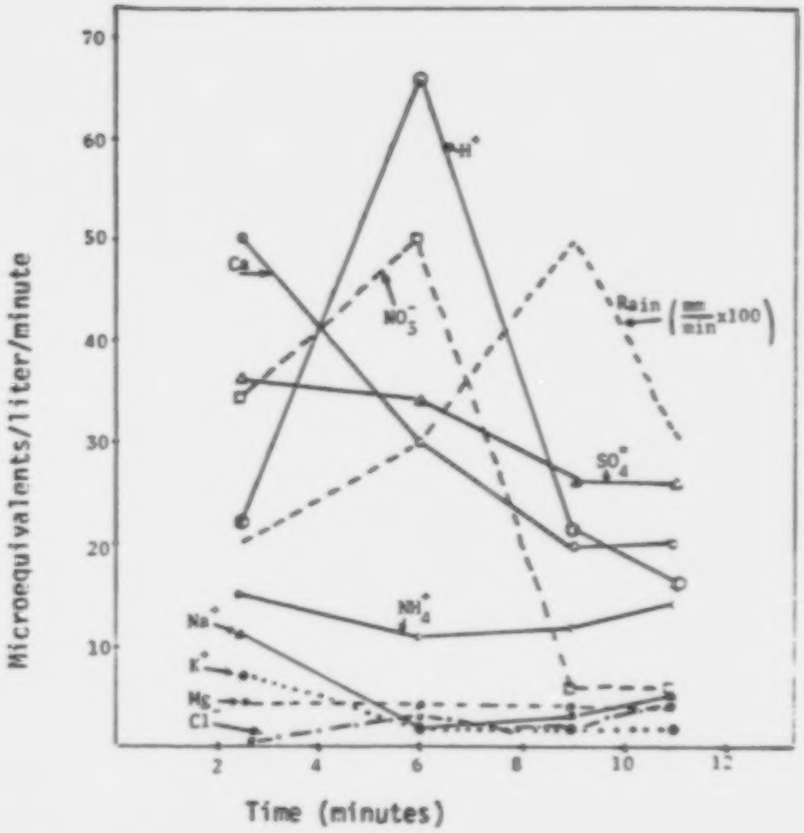


Figure 11. Composition of rain during sequential sampling. Red Deer-Rocky Mountain House. 17 July 1978.

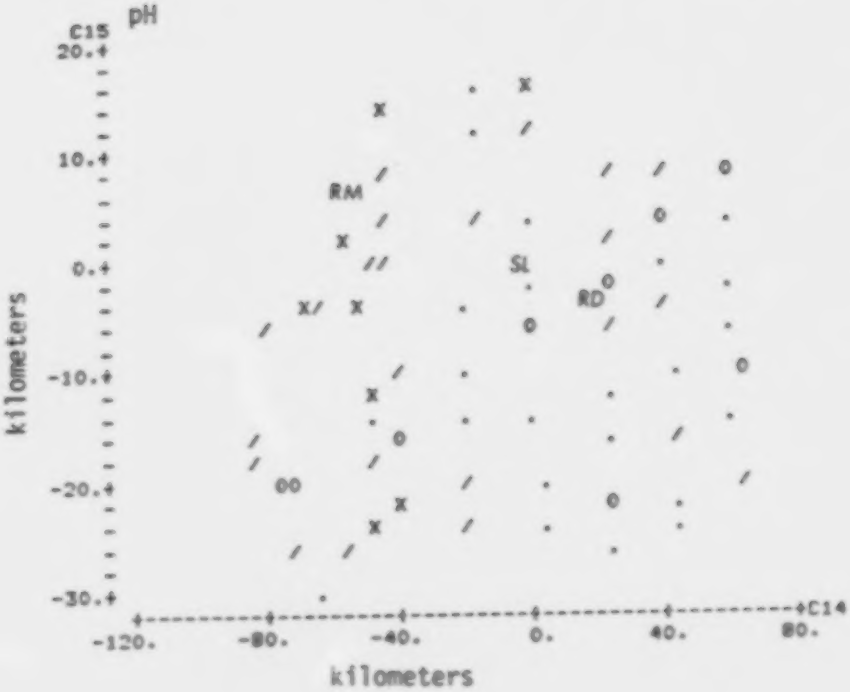


Figure 12. Geographical distribution of pH. Total snow depth. Red Deer-Rocky Mountain House.

O DENOTES VALUES L.T. 5.06184
. DENOTES VALUES L.T. 5.75175
/ DENOTES VALUES L.T. 6.44165
X DENOTES VALUES G.T. 6.44165

RM - ROCKY MOUNTAIN HOUSE
RD - RED DEER
SL - SYLVAN LAKE

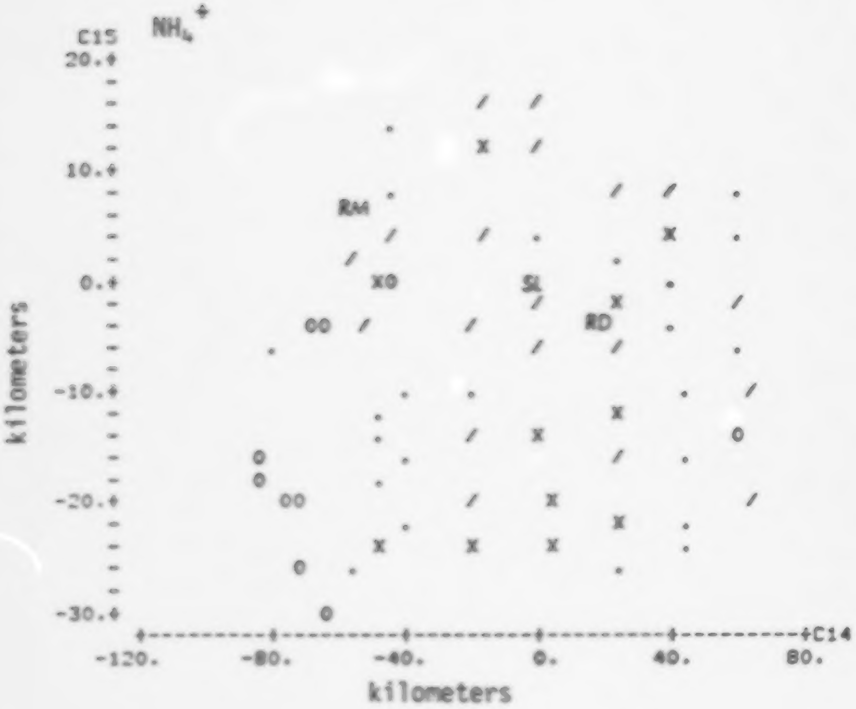


Figure 13. Geographical distribution of NH_4^+ concentrations (mg/L). Red Deer-Rocky Mountain House. Total snow depth.

O DENOTES VALUES L.T. 0.11144
. DENOTES VALUES L.T. 0.24127
/ DENOTES VALUES L.T. 0.37110
X DENOTES VALUES G.T. 0.37110

RM - ROCKY MOUNTAIN HOUSE
RD - RED DEER
SL - SYLVAN LAKE

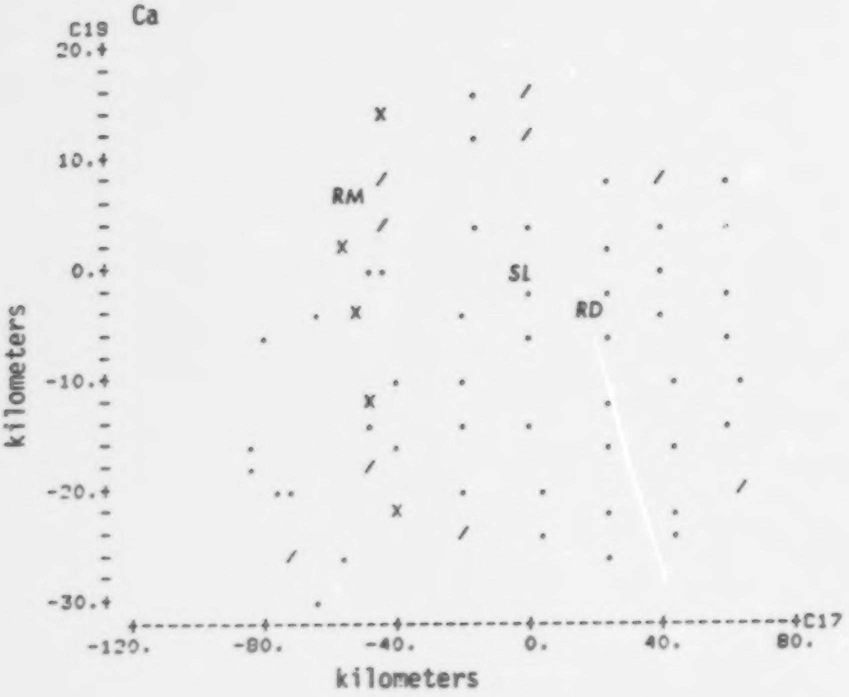


Figure 14. Geographical distribution of Ca concentrations (mg/L). Red Deer-Rocky Mountain House. Total snow depth.

O	DENOTES VALUES	L.T.	-0.03845
.	DENOTES VALUES	L.T.	0.64557
/	DENOTES VALUES	L.T.	1.32959
X	DENOTES VALUES	G.T.	1.32959

RM - ROCKY MOUNTAIN HOUSE
RD - RED DEER
SL - SYLVAN LAKE

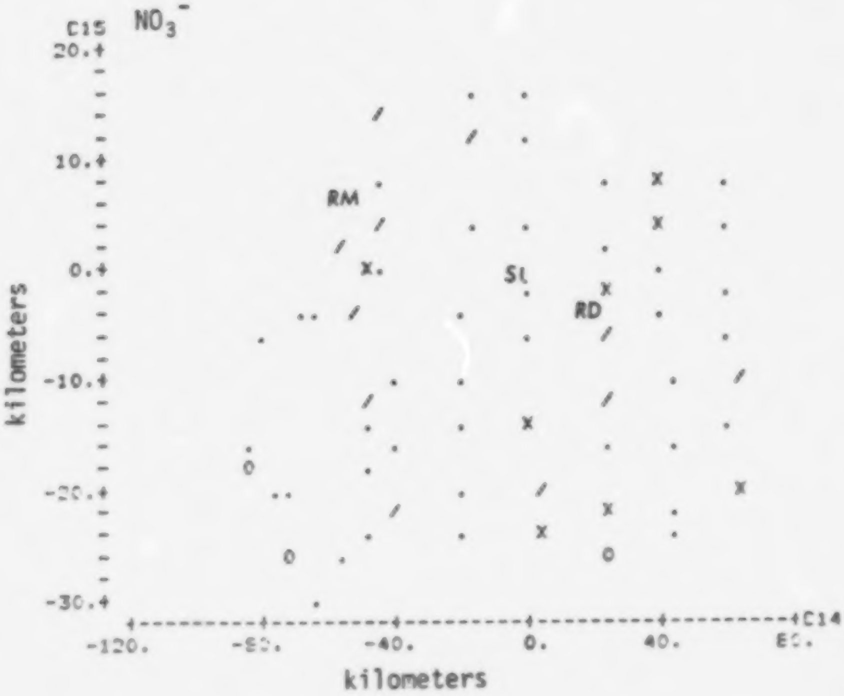

NO3-
C15
20.
10.
0.
-10.
-20.
-30.
kilometers
RM
SL
RD
C14
-120.
-80.
-40.
0.
40.
80.
kilometers

Figure 15. Geographical distribution of NO_3^- concentrations (mg/L). Red Deer-Rocky Mountain House. Total snow depth.

O DENOTES VALUES L.T. 0.68249
. DENOTES VALUES L.T. 0.94873
/ DENOTES VALUES L.T. 1.21497
X DENOTES VALUES L.T. 1.21497

RD - RED DEER
RM - ROCKY MOUNTAIN HOUSE
SL - SYLVAN LAKE

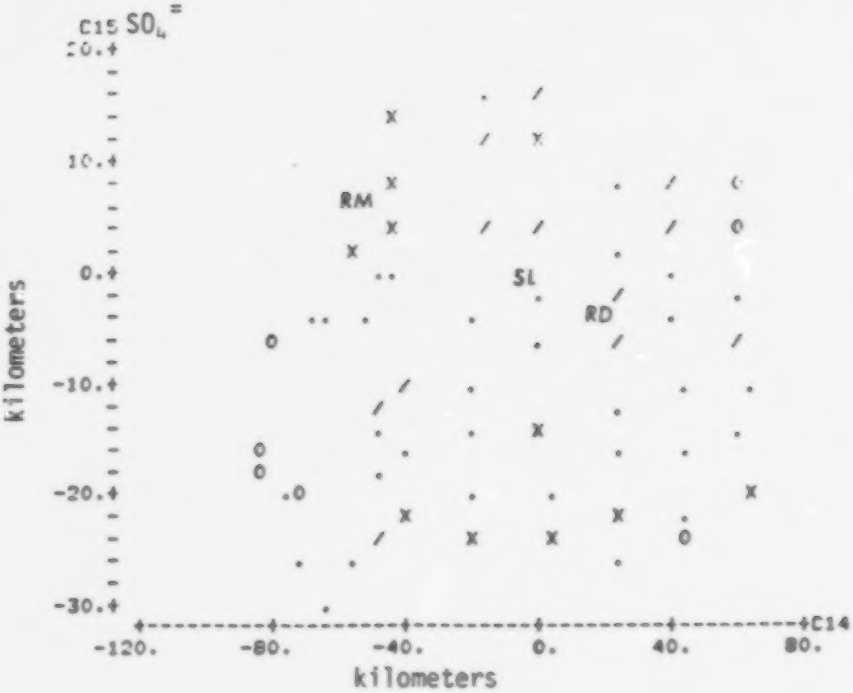

C15 $SO_4^=$
20.
10.
0.
-10.
-20.
-30.
kilometers
RM
SL
RD
C14
-120.
-80.
-40.
0.
40.
80.
kilometers

Figure 16. Geographical distribution of $SO_4^=$ concentrations (mg/L) in total snow depth. Red Deer-Rocky Mountain House.

O	DENOTES VALUES L.T.	0.62417	RD - RED DEER
.	DENOTES VALUES L.T.	0.94032	RM - ROCKY MOUNTAIN HOUSE
/	DENOTES VALUES L.T.	1.25646	SL - SYLVAN LAKE
X	DENOTES VALUES L.T.	1.25646	

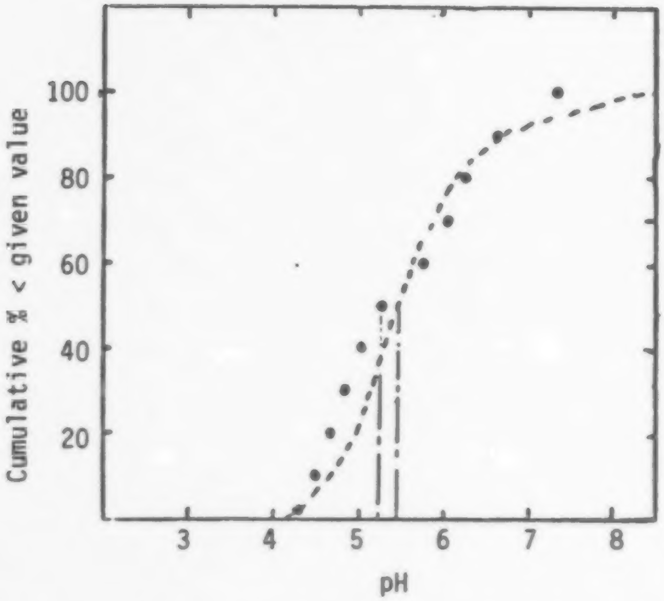


Figure 17. Accumulative percent of pH less than indicated value.

PLUME CHEMISTRY STUDIES DURING 1980 IN THE ATHABASCA TAR SANDS AREA

J.W. BOTTENHEIM[1]

Abstract

During the winter and summer of 1980, plume chemistry studies were undertaken to obtain information on the transformation chemistry of SO_2 and NO_x, emitted by the tar sands plants in northern Alberta. In this paper, the scope of the data obtained is described, and the results are analyzed with respect to the oxidation mechanisms of SO_2. It appears that liquid phase chemistry is responsible for sulphate formation in the winter, equally producing sulphate. Data on NO_x and HNO_3 are very limited but do suggest that HNO_3 is formed. Hydrocarbon levels observed were in the low ppb range, and were suspected to originate at the tar sands plants only. Nevertheless, excess ozone formation in the plumes was observed in the summer.

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[1] Atmospheric Environment Service, Downsview, Ontario

1. INTRODUCTION

Burning of fossil fuels for energy production is not a pollution free process; waste gases are produced such as sulphur dioxide (SO_2) and oxides of nitrogen (mainly nitric oxide, NO, nitrogen dioxide, NO_2). In recent years it has become clear that these atmospheric pollutants can be transformed into sulfuric acid (H_2SO_4) and nitric acid (HNO_3). These so called strong acids are believed to be largely responsible for the problem of acidified precipitation. Furthermore, concurrently with these transformations, oxidants such as ozone (O_3) and peroxyacetylnitrate (PAN) can be produced. All these so called secondary pollutants are believed to ultimately have a detrimental effect on the terrestrial and aquatic environment.

Extensive laboratory and field work during the last decade has elucidated some of the major features of this transformation chemistry. Abundant evidence suggests that both homogeneous and heterogeneous pathways of transformation occur in the atmosphere. Homogeneous oxidation in the gas phase mainly involves reactions with OH radicals produced from photochemical reactions and hence requires near UV radiation from the sun as initiator. Liquid phase oxidation takes place after the reactants are dissolved in cloud or aerosol droplets. The actual oxidation that follows is as yet poorly understood, but presumably involves oxidizing species such as hydrogen peroxide (H_2O_2) or O_3, or catalyzing metal ions. It is painfully clear from the abundance of field study results, that beyond such general features, sufficiently unique aspects are associated with each polluting source so that prediction of the actual transformation chemistry is a hazardous undertaking without an extensive body of on-site observations.

The Alberta Oil Sands Environmental Research Program (AOSERP) was initiated in order to assess the environmental impact of future development near the Athabasca oil sands deposit. It was realized early in the program that the atmospheric chemistry in the region had to be known for such an assessment. Hence, during 1977 and 1980, the major exhaust plumes in the region have been investigated by aircraft monitoring, and a theoretical model has been developed. Reports on the 1977 field studies and plume chemistry modelling have appeared in the AOSERP monograph series (Fanaki 1979a, 1979b; Bottenheim and Strausz 1981). This paper will report results from the 1980 field studies, and discuss the transformation chemistry of SO_2 into sulphate ($SO_4^=$), based on these data.

2. OVERVIEW OF THE 1980 FIELD STUDIES

The 1980 plume chemistry field studies were specifically initiated to study the potential for transformation of major emitted pollutants(SO_2 and NO_x) into acidic secondary components (H_2SO_4 and HNO_3 respectively). A small airplane was instrumented to monitor the plumes from the Syncrude, and to a lesser extent, Suncor plants, at progressively longer plume travel time under different seasonal conditions. In this section an overview of the sampling program and a summary of the data obtained will be presented.

2.1 METEOROLOGICAL CONDITIONS

Three sampling campaigns were held: January 9-13, March 18-25 and June 28 - July 8. The January period was characterized by extreme cold winter conditions (typically -20° to -30° C at the surface) with strong inversions aloft.The plume conditions were generally very similar with very little vertical mixing. There were no cases with the plumes penetrating the inversion level, nor were there any cases of fumigation mixing down to the surface. On one particular day (January 10) the plume was emitted into a clearly noticeable ice fog. Although some highly interesting results were obtained during this day, they will not be discussed here.

The March campaign took place under more moderate, late winter conditions with surface temperatures a few degrees below freezing. Plume behaviour was again rather constant with more vertical mixing than in January, but still in a stable boundary layer. Only on March 25 was the plume sampled in a neutral boundary layer, and was there some evidence of plume fumigation.

During June/July quite different climatic conditions were encountered with typical summer type weather (largely sunny weather with some afternoon scattered cloud and surface temperatures in the mid 20°C). The synoptic conditions then ranged from stable boundary layers that resulted from nocturnal inversions to mid-afternoon convective instabilities. On several occasions plume fumigation to the surface was apparent.

2.2 IN SITU MONITORING

Several parameters were continuously monitored on board while traversing the plumes. It was intended to record all useful data on magnetic tape, however, for a variety of reasons such recording failed during each campaign. Hence traces from gas monitors were obtained on backup chart recorders, while other parameters were tabulated as average values observed by the instrument operator during each flight. A list of in situ parameters thus monitored is presented in Table 1, while figure 1 shows a representative set of chart recorder traces. Note that no radio signals were used for establishing the sampling location. The accuracy of such a procedure based on available radio signals in the AOSERP area was deemed less than could be obtained by visual observations.

The traces of the gas monitors were used for plume identification, and estimation of the SO_2/NO_x ratio. The ratio observed ranged from ca. 5:1 to 10:1 as would be expected from the emission data of the Syncrude and Suncor plant (Shelfentook 1978). On occasion, though, relatively more NO_x was observed. The

Table 1. In situ monitoring equipment.

Temperature	Rosemont 102u2u	-50°C to 50°C	± 0.5°C
Dew Point	E.G. & G. model 137	-50°C to 50°C	± 0.5°C
Atmospheric Pressure	Ball model Ex 410	$0-30,000^{1}$MSL	$\pm 75^{1}$
Air Speed	Ball model Ex 210	0-200 KIAS	± 2KTS
SO_2	Meloy model SA285	0.5 - 1000 ppb	± 0.5 ppb
$NO - NO_x$	Monitor Labs, model 8440E	2 ppb - 5 ppm	± 1%
O_3	Monitor Labs, model 8410A	3 ppb - 20 ppm	± 1%
Data Acquisition	Monitor Labs, model 9400 MFE Chart Recorders		

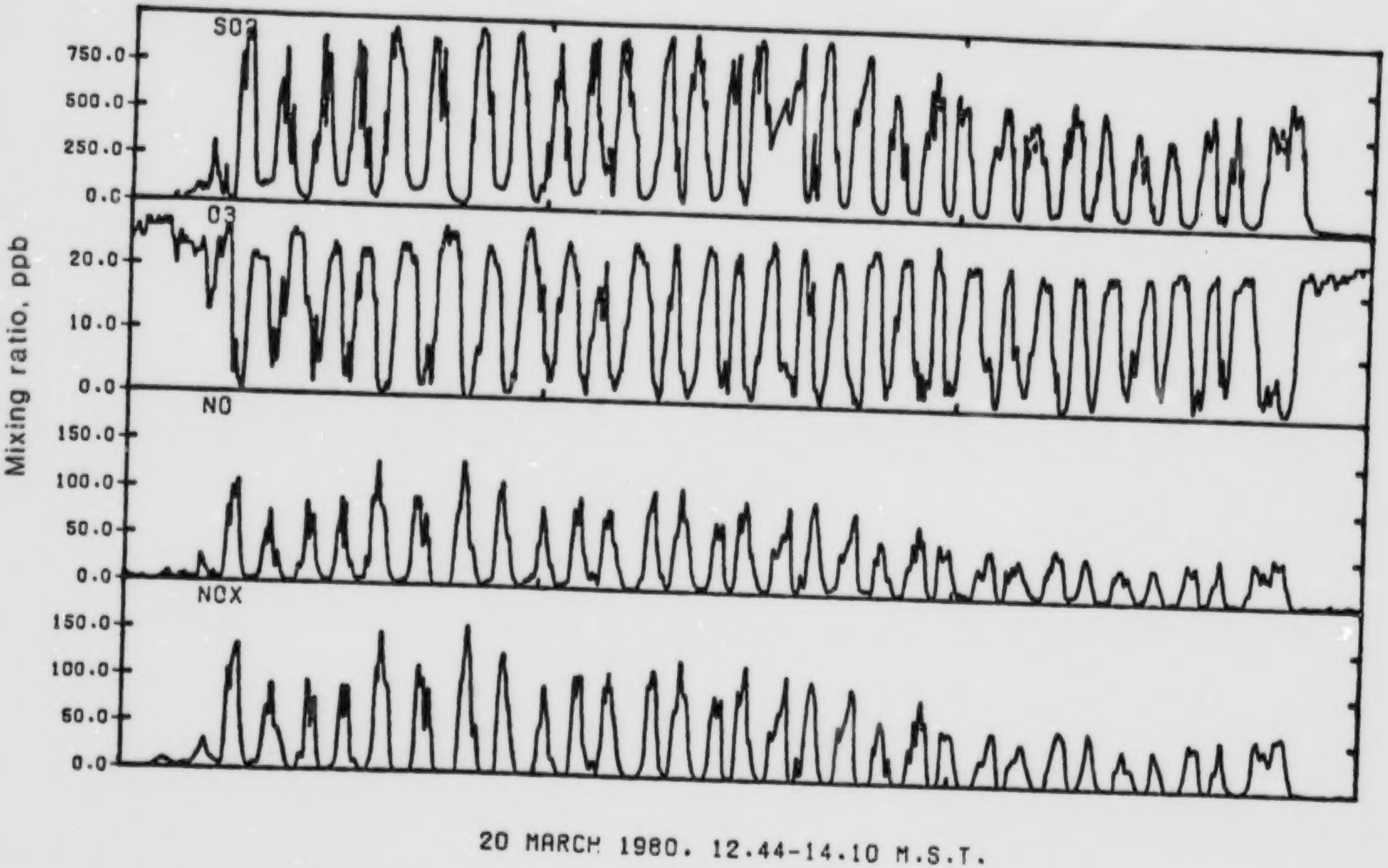

Figure 1. Chart recorder traces of gas monitors during sampling of Suncor plume.

SO_2/NO_x ratio was observed to change with plume travel time, but no consistent trend seems to emerge from these data.

Quantitatively, the maximum values for SO_2 and NO_x ranged from ca. 1 and 0.2 ppm respectively close to the chimney to below detection limit (estimated at 10 ppb each for SO_2 and NO_x) in the background air. O_3 on the other hand ranged from essentially zero at the plume centre close to the stack, to ambient levels of ca. 18, 25 and 50 ppb during January, March and July respectively. The occurrence of excess ozone levels was occasionally observed during July within the plume boundaries at ca. 15 - 20 miles downwind from the chimney. These results were not unexpected in view of similar observations by Lusis et al. (see Fanaki 1979b), but remain difficult to rationalize since sufficient hydrocarbons to promote excess ozone formation were not observed. Additional data on the levels of oxides of nitrogen, and the NO_2/NO ratio, would be very instructive in delineating the origin of excess ozone, but with commercially available instrumentation it is doubtful that the required sensitivity can be attained to make such measurements. Certainly with the equipment available during these field studies, measurements of NO and NO_2 at levels of 1 ppb or less were impossible.

2.3 FILTER PACK COLLECTIONS

Filter packs were employed to obtain data on the average levels of particulate sulphate and nitrate, and gaseous nitric acid and sulphur dioxide. This sampling method followed identical procedures as described in detail by Lusis et al. (see Fanaki 1979a) with the following modifications.

The front part of the Swinnex filter holder was replaced by an identical part, made of Teflon, and a 3 um pore diameter Teflon filter was used for particulate sampling. Next an extra stage was added before the filters that would collect SO_2. This extra stage was also made of Teflon, and lead to a NaCl impregnated Whatman-41 filter, which was intended to collect gaseous HNO_3. The switch to an all-Teflon front part was made to minimize potential interference with sampling HNO_3 (Stevens 1979). No specially designed isokinetic sampling tip was used, and the air was sampled at a rate of ca 20 $l.min^{-1}$ by means of a Venturi exhaust at the end of the sampling line. The sampling rate was measured after the filter holder but before the Venturi using a Hastings mass flow meter. All exposed filters were stored in petri-dishes and as soon as possible shipped to Edmonton, where they were analyzed by ion chromatography at the Alberta Research Council.

It turned out that with the way sampling was performed, the amount of sulphate collected on the particulate filter was often barely enough for analysis purposes. It is therefore not surprizing that no detectable amount of HNO_3 was ever observed on the second filter, since the expected sulphate/nitrate (including HNO_3) ratio is larger than 1. Hence during the March and June/July campaign occasionally the air was sampled with a Hi-vol sampler on Whatman-40 filters. On these filters one would expect to collect all sulphate particles as well as most nitrate, including gaseous HNO_3. Although the sampling arrangement was far from ideal, the data obtained show the intuitively expected trend of increase of nitrate/sulphate ratio with plume travel time; the nitrate/sulphate ratio ranged from less than 0.1 to ca. 0.3. Current understanding of the oxidation chemistry of NO_x and SO_2 suggests that the $NO_x \rightarrow HNO_3$ transformation occurs more rapid than the $SO_2 \longrightarrow H_2SO_4$ transformation. Hence one would expect the nitrate/sulphate ratio to increase with plume travel if both nitrate and sulphate are produced after emission of NO_x and SO_2 respectively.

2.4 GRAB SAMPLING FOR HYDROCARBON ANALYSIS

Earlier field studies in the AOSERP study area indicated the possibility of homogeneous gasphase conversion of SO_2 into sulphate. Hence it was decided to collect grab samples of plume and background air during the 1980 field studies, and determine whether measureable amounts of reactive hydrocarbons were present that could stimulate such gas phase chemistry. Grab samples of air were collected in Tedlar bags, shielded from sunlight by two layers of black garbage bags. The sampling system consisted of a 1/4" stainless steel line, and the bags were filled with ram air, thus avoiding potential contamination from pumps. The grab samples were analyzed by gaschromatography (HP-5830 GC; Porapak-N for C_2 and Durapak/n-octane for C_3-C_6 hydrocarbons) usually immediately after termination of each flight at the AOSERP Mildred Lake facilities in order to minimize potential sample deterioration.

In agreement with literature data (Chameides and Cicerone 1978; Cronn and Robinson 1979) the background air was found to be almost totally devoid of hydrocarbons (excluding methane), with only small levels of ethane and acetylene present (ca. 1 ppbC each). Within the plume boundaries some hydrocarbons were found that obviously originated from the plants since their concentration dropped rapidly with distance from the chimney. Most of these compounds (ca. 90%) were paraffins; this is a further indication that the origin of these compounds is at the tar sands plants, presumably from the flare stack and evaporative emission of refinery operations (Sexton and Westberg 1979). However, even close to the chimney, the total amount observed was usually of the order of 30-50 ppbC only. Moreover, paraffins have at most a moderate potential for sustaining OH-radical type chemistry. Hence serious doubt remains whether these hydrocarbons could have caused the excess ozone levels observed during the summer field studies of 1977 and 1980. Some qualitative evidence for the presence of aromatic hydrocarbons (for which no analysis could be performed during 1980) was found, and this might have been the agent responsible for the excess ozone effect (Bottenheim and Strausz 1981).

3. THE TRANSFORMATION MECHANISM OF SO_2 IN THE AOSERP AREA

Field experiments outside the sheltered laboratory environment will always suffer from many uncontrollable factors that severely influence the intended observations. Data from such experiments can sometimes be used to obtain quantitative conclusions by filtering out those results that are obviously biased by factors not relevant to the goals of the study. The 1980 field studies in the Tar Sand area have yielded a data set that seems too sparse to allow for such a procedure. Hence, in Table 2 the total data set on SO_2 and sulphate observations as obtained from filter pack sampling is presented. Qualitative trends concerning the plume chemistry in the area will be derived from these results.

3.1 DATA CONSISTENCY

Two independent methods were employed to determine SO_2 levels in the plume. Filter packs registered the average concentration of SO_2 and sulphate at each sampling location. Concurrently a flame photometric detector (FP-analyzer) recorded instantaneous SO_2 levels thus showing the plume profile. Integration of the surface under the curves yields an independent estimate of the average SO_2 concentration. A comparison of the two methods indicated slightly higher levels from the FP analyzer than the filter pack during the winter. Although the scatter is rather large, such a trend concurs with similar observations elsewhere (Anlauf, private communication). It could be concluded that the collection efficiency for SO_2 by Whatman-41 filters, impregnated with K_2CO_3/glycerol is somewhat less than total at low temperatures. However, the deviation is small, and combined with the data scatter, is most likely not significant. Hence it is concluded that the filter pack data are as reliable as can be expected from such experiments. Unfortunately a similar comparison for the summer data is much worse, and shows the opposite trend, Table 2. $SO_4^=$/total-S ratio as determined by filter pack sampling during 1980 plume chemistry field studies.

Date	Source[a]	Distance (mi)	Time[b] (MST/MDT)	Wind[c] (mph)	Temp. (^oC)	Dew Point (^oC)	Plume Travel Time (min)	$SO_4^=$/total-S[d] (%)	$\Delta[SO_4^=/total-S]$ ($\%\cdot h^{-1}$)
9-1-80	Sy	4	18:17-18:38	15-17	-23	-	15	14.7	
		6	17:55-18:15				23	17.9	24
11-1-80	Sy	2	13:57-14:19	10-12	-26	-	11	18.3	
		8	14:30-15:02				44	26.4	14.7
		15	15:40-16:15				82	17.0	-15.7
	Su	10	15:05-15:31				55	5.5	
13-1-80	Sy	2	11:06-11:30	12-14	-20	-	9	8.8	
		10	11:39-12:11				46	13.3	7.3
		20	12:16-12:51				92	10.4	-3.8
		30	15:45-16:18				138	13.4	3.9
18-3-80	Sy	2	15:45-16:51	14-16	-3	-	8	10.7	
	Su	2	17:02-17:35				8	3.2	
19-3-80	Su	2	17:28-18:08	6-8	-2	-	17	7.5	
		11	18:20-19:16			-	94	4.2	-2.6
20-3-80	Sy	2	11:12-12:30	3-5	-6.5	-	30	6.4	
	Su	2	12:38-14:10				30	1.6	

Continued..

Table 2. (continued)

Date	Source[a]	Distance (mi)	Time[b] (MST/MDT)	Wind[c] (mph)	Temp. (°C)	Dew Point (°C)	Plume Travel Time (min)	$SO_4^=$/total-S[d] (%)	$\Delta[SO_4^=/\text{total-S}]$ ($\%\cdot h^{-1}$)
21-3-80	Sy	2	12:25-13:51	3-5	-4.5	-	30	7.7	
		8	14:02-15:31				120	2.5	-3.5
		20	17:15-18:49				300	2.1	-0.1
24-3-80	Sy	2	10:13-11:30	16-18	-3	-	7	1.2	
		2	11:40-13:15				7	1.1	
25-3-80	Sy	2	10:10-11:10	9-11	-7	-	12	2.6	
		6	13:14-1400				60	3.8	1.5
		25	14:25-15:20				250	2.9	-0.3
28-6-80	Sy	1	12:50-13:45	N.D.[e]	17	6	N.D.	1.8	
	Su	1	14:20-15:03		17.5	6		2.1	
4-7-80	Sy	1	10:10-11:11	4-6	21.5	8.5	12	1.3	
		5	11:20-12:25		19.5	8	60	3.4	2.6
5-7-80	Sy	1	8:00-8:35	8-10	19	11	7	0.8	
		5	6:50-7:55		18.5	11	33	1.2	0.9
		35	5:15-6:45		20	11.5	233	0.7	-0.7
7-7-80	Sy	6	5:30-6:30	8-10	16	4.5	40	1.5	
			10:40-11:25		18	6	40	1.1	
			14:45-16:00		21	12	40	5.7	
			18:38-19:28		22.5	10.5	40	13.6	

Continued..

Table 2. (concluded)

Date	Source[a]	Distance (mi)	Time[b] (MST/MDT)	Wind[c] (mph)	Temp. (°C)	Dew Point (°C)	Plume Travel Time (min)	$SO_4^=$/total-S[d] (%)	$\Delta[SO_4^=/\text{total-S}]$ (%·h⁻¹)
7-7-80	Sy	1	11:30-12:00	8-10	18.5	11	6.7	0.9	
		6	10:40-11:25		18	6	40	1.1	0.4
8-7-80	Sy	1.5	11:30-11:59	N.D.	18	8.5	N.D.	3.6	
		6	10:45-11:25		18.5	9		3.1	N.D.

NOTES:

a Sy = Syncrude, Su = Suncor

b MST in January, March; MDT in June, July

c No inflight measurements were made; data derived from Fort McMurray airport soundings

d Accuracy is estimated at 25%

e N.D. = no data available

viz. more SO_2 was found on the filters than suggested by the FP analyzer. This observation is almost certainly due to less reliable data from the FP analyzer. (The summer study used a different instrument that caused several problems not encountered during the winter).

3.2 PERCENT SULPHUR AS SULPHATE

It can be seen in Table 2 that the percent sulphur as sulphate (the SO_4/total-S ratio) appears to increase markedly during some of the January samplings, and less so during one March and one July sampling with plume travel time. Otherwise, several cases of a decrease in the SO_4/total-S ratio is observed. Although the error limits are believed to be large, the observed variations are too large to be due to such errors and hence are considered significant. On several occasions Newman and co-workers have observed a similar decrease in the SO_4/total-S ratio at longer plume travel time when sampling power plant plumes in the United States (Newman et al. 1975a, 1975b; Forrest and Newman 1977). These workers also found evidence that sulphate particles actually dropped out of the plume. Similarly Barrie (1980) observed the phenomenon of "snowout" from the Suncor plume during winter field studies in the AOSERP study area. Although no direct evidence for such a loss of sulphate was observed during the 1980 studies, most likely it is the explanation for the decrease in the SO_4/total-S ratio.

Worth noticing is the generally large percentage sulphur as sulphate in the Syncrude plume, particularly during January. Lusis et al. (in Fanaki 1979a,b) observed an average level of only ca. 1-2% in the Suncor plume during their field studies. At first thought one is tempted to conclude that the observation on the Syncrude plume is due to incomplete collection of SO_2 on the filters (see the discussion above). However, one sampling of the Suncor plume was made in January, and it shows an SO_4/total-S ratio reasonably in agreement with the data from Lusis et al. Subsequently during March and June, time was devoted to a more determined comparison between Syncrude and Suncor and often the initial SO_4/total-S ratio was observed to be higher in the Syncrude than the Suncor plume. The reason for this fact is not clear, but it should be caused by differences in plant operations between Syncrude and Suncor.

3.3 TRANSFORMATION OF SO_2 TO SULPHATE DURING THE WINTER

Contrary to the results obtained by Lusis et al. in 1977, when studying the Suncor plume, the data from the 1980 field studies suggest that some transformation of SO_2 to sulphate does occur during the winter in the Syncrude plume. The largest apparent conversion was observed during a very cold early night flight (January 9), and hence if these data do indeed mean an oxidation of SO_2 to sulphate, then a photochemically induced process is not responsible. Furthermore, an increase in the SO_4/total-S ratio is only observed during the first hour of plume travel. In particular, the only increase in this ratio observed during the March sampling period coincides with the only occasion that the second observation point was reached by the plume after less than one hour of travel. Finally all increases in the SO_4/total-S ratio were observed on days with temperatures below 0°C. The magnitude of this increase seems to correlate inversely with temperature, with the largest increase occurring at the lowest temperatures. These observations are in agreement with the theoretical treatment of Freiberg (1976) concerning the iron catalyzed oxidation of SO_2 in a power plant plume. It might be added here that analysis of fly ash from the Syncrude chimney shows that iron is by far the most abundant metal present.

One might argue that the observed changes in the SO_4/total-S ratio were due to other factors not related to transformation. Thus the initial increase in the ratio followed by subsequent decrease might be due to the opposing effects of more effective collection of SO_2 at lower average concentration and decreased importance of sulphate fall out at longer travel times. Such an explanation cannot be ruled out, but seems rather coincidental. Furthermore, it would suggest a much larger problem with the SO_2 collection efficiency than seems apparent and finally seems at odds with the "normal" SO_4/total-S ratio observed during January in the Suncor plume.

3.4 TRANSFORMATION OF SO_2 TO SULPHATE DURING THE SUMMER

At first sight the data of July 4, 7 and 8 would allow for an analysis of summer daytime transformation of SO_2. However, the absence of an apparent conversion during July 7 and 8 is probably due to other factors than the absence of oxidation. There is good evidence that the two sampling periods occurred during different meteorological regimes. Thus the first sampling, which on both days took place between 10 and 11 A.M., concurred with the break up of the nighttime inversion and the plume did not yet touch the surface while the second sampling occurred well after the onset of fumigation. Pertinent temperature profiles are not available, but two other pieces of information substantiate this observation. Firstly, on both days the second sampling location was closest to the chimney and yet the amount of sulphur collected on the filters, as well as the maximum SO_2 concentration indicated by the FP analyzer, was substantially lower than found during the first sampling. Secondly, during these field studies it was determined that acetylene (C_2H_2) levels generally indicated plume dilution and stability. Thus, markedly elevated C_2H_2 levels were usually observed after relatively short plume travel time ($<$ 1 hour) when little plume dilution would be expected, viz. in the winter or at very early morning hours in the summer, at low wind speeds. On both July 7 and 8, C_2H_2 levels were substantially higher during the first sampling period than the second, while on July 4 the C_2H_2

levels were of comparable order of magnitude, and higher at the observation point closest to the chimney (see Table 3).

The data obtained on July 4 suggest a transformation rate of SO_2 of 2.6%·h^{-1}. Such a rate is entirely in line with many other field studies (for recent work see Atmospheric Environment, Vol. 15, no. 10-11, 1981). It is also in agreement with the data reported by Lusis et al. for the Suncor plume. During the very early morning flights of July 5 and 7, all sampling occurred also in the same meteorological regime, viz. before inversion break-up (see C_2H_2 levels, Table 3) but no significant change in SO_4/total-S ratio was observed as function of plume travel time.

Contrary to observations during the winter, these data then once more suggest that photochemically initiated oxidation of SO_2 takes place. One of the goals of the 1980 field studies was to determine whether otherwise the atmospheric composition was conductive to such an oxidation mechanism of SO_2, and hence hydrocarbon levels were determined. The hydrocarbon content during the samplings of July 4 is shown in Table 4. Abnormally high propane levels seem to be present (abnormally high in comparison with observations on most other days), but otherwise hydrocarbon concentrations are quite low, particularly in background air. If the data on propane are real, then the levels observed would certainly be sufficient to sustain the necessary OH radical concentration, but it is more likely to be an artifact. If so, a sufficient level of hydrocarbons would appear to be marginally present, and probably a few ppbC of aromatic hydrocarbons and/or aldehydes would have to be present as well to create sufficient OH radicals (Bottenheim and Strausz 1981). On the other hand, photochemical activity is often indicated by elevated ozone levels, downwind within the plume boundaries. No such indications were looked for on July 4, but both on July 7 and 8 evidence for elevated ozone levels was found at distances of beyond 10 miles from the chimney (see Figure 2.).

Table 3. C_2H_2 levels during July, 1980

Day	Time (MDT)	Distance from Syncrude chimney (mi)	C_2H_2 (ppb C)
4-7-80	10:30	1	2.1
	11:50	5	1.1
	12:50	Background	0.4
5-7-80	06:00	35	20.7
	07:00	5	10.3
	08:00	1	22.9
7-7-80	06:00	6	10.9
	07:30	Background	1.6
	11:00	6	9.3
	12:00	1	1.6
	15:00	6	0.7
	18:30	6	0.6
8-7-80[a]	11:00	6	40.3
	11:45	1.5	11.0
	14:00	15[b]	1.2
	15:30	8[b]	2.6

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[a] These samples were analyzed on 11-7-80 in Edmonton.

[b] Suncor plume sample; distance from Suncor chimney.

Table 4. Light hydrocarbons during July 4, 1980[a].

Location	1	2	3
ethane	8.5	6.5	5.2
ethylene	6.1	5.0	1.2
acetylene	2.1	1.1	0.4
propane	162.0	53.8	31.7
propene	2.5	1.2	T
i-butane	3.4	1.8	0.7
n-butane	8.6	5.6	1.2
1-butene	1.2	0.9	--
i-butene	0.8	6.8	T
t-2-butene	T	T	--
i-pentane	4.9	3.5	T
n-pentane	9.5	7.2	T
cyclopentane	2.7	3.0	--
1-pentene	T	T	--
2-m-pentane 3-m-pentane m-cyclopentane n-hexane cyclohexane	98.6	N.D.	10.7

Number	Location	Sampling Time (MDT)
1	Syncrude plume, 1 mi	10:30
2	Syncrude plume, 5 mi	11:50
3	Background	12:50

[a] All mixing ratios in ppbC; T = trace; N.D. = not determined.

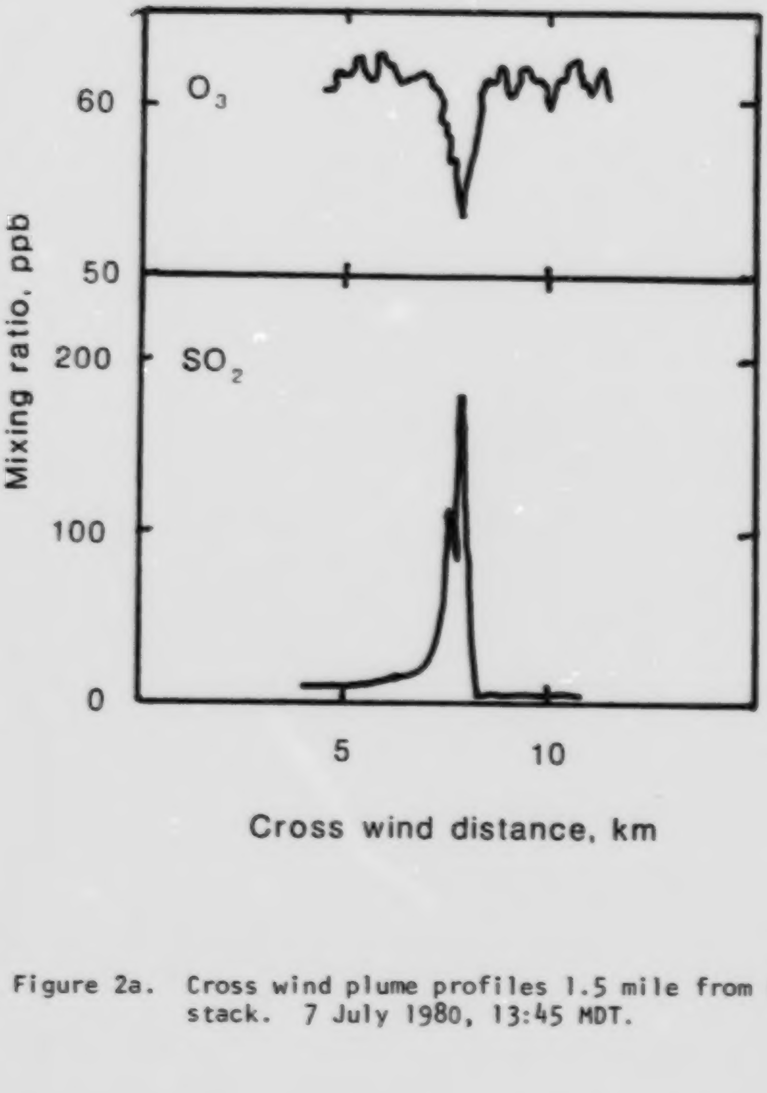

Figure 2a. Cross wind plume profiles 1.5 mile from the Syncrude stack. 7 July 1980, 13:45 MDT.

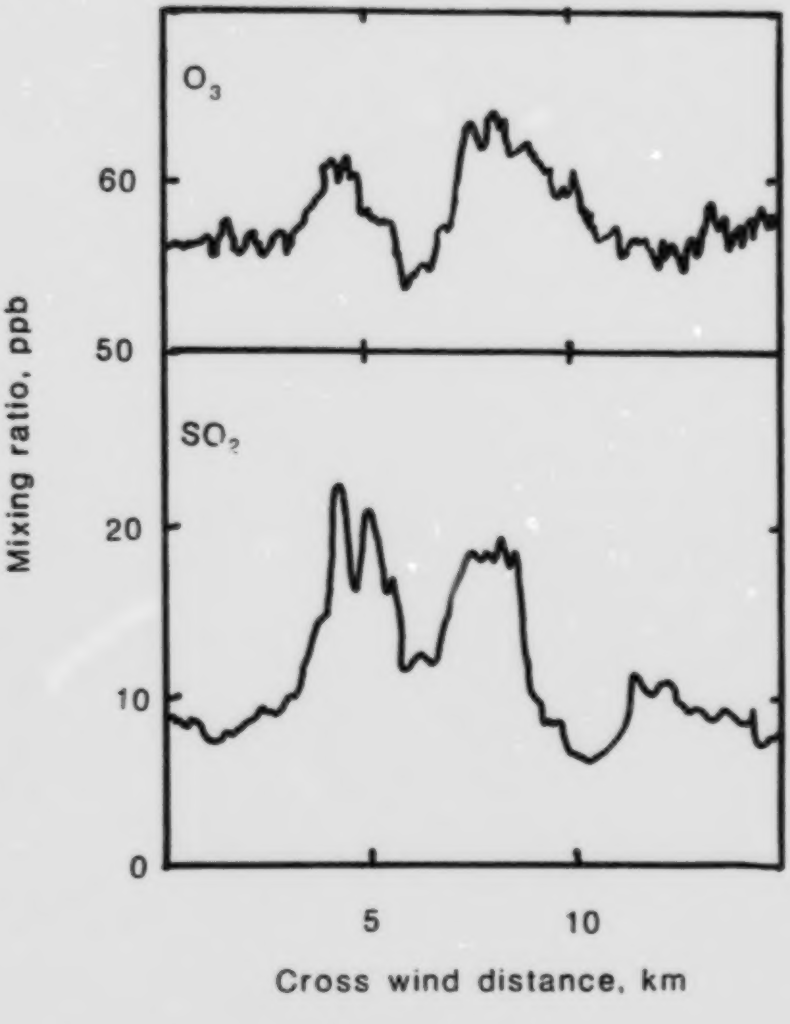

Figure 2b. Cross wind plume profiles, 12 miles from the Syncrude stack. 7 July 1980: 14:10 MDT.

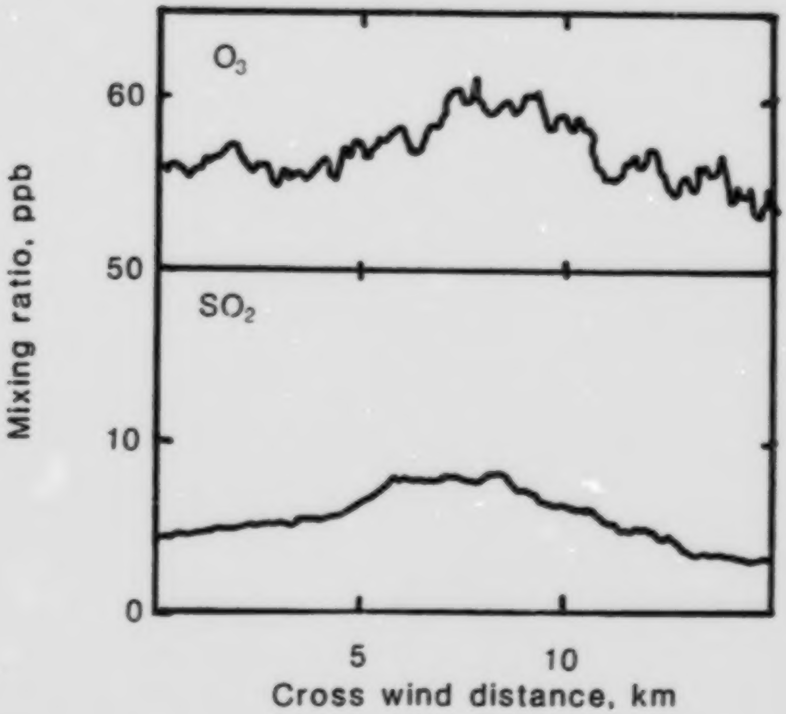

Figure 2c. Cross wind plume profiles, 20 miles from the Syncrude stack. 7 July 1980, 14:20 MDT.

4. SUMMARY AND CONCLUSIONS

The 1980 plume chemistry field studies in the AOSERP study area were undertaken to obtain information on the transformation chemistry of SO_2 and NO_x emitted by the tar sands plants. An overview of the scope and results of the study was presented in this paper. It was indicated that data obtained in the winter suggest that during the first hour of plume travel transformation of SO_2 into sulphate does occur. Such an oxidation could not be due to homogeneous gas phase chemistry and in fact several observations conformed to the iron-catalyzed oxidation mechanism in the liquid phase, proposed by Freiberg (1976). Data obtained in the summer, however, suggest a homogeneous gas phase oxidation mechanism; although insufficient reactive hydrocarbons were identified, excess ozone within the plume boundaries supported this analysis.

As far as NO_x is concerned, few data were obtained largely due to instrument limitations. No consistent trend with plume travel emerged from the SO_2/NO_x ratio, but the few data on the nitrate/sulphate ratio were qualitatively in agreement with expectations and suggested that HNO_3 formation does indeed take place in the plumes from the tar sands plants, albeit at low levels. Such a conclusion has to be very tentative at present due to the very limited amount of data, but suggests that future studies in the area should attempt to monitor HNO_3 as well as the sulphates.

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SULPHUR ISOTOPE TRACING OF ACID FORMING EMISSIONS INTO THE ENVIRONMENT IN ALBERTA

H.R. KROUSE[1] AND J.W. CASE[1]

ABSTRACT

Sulphur emissions from gas processing plants in Alberta are significantly enriched in the heavier sulphur isotope ^{34}S as compared to the surrounding environment. This "isotopic leverage" is a powerful technique for tracing sulphur compounds of industrial origin throughout ecosystems. Data from the atmosphere, hydrosphere, biosphere and pedosphere are cited for locations which have experienced sulphurous emissions ranging from almost negligible through to over 20 years of significant exposure. These data are synthesized into two composite diagrams which assess the contributions of industrial sulphur compounds to the environment. In one diagram, the influx of industrial sulphur is documented by plotting the $\delta^{34}S$ values of leaves against those of the soil. In the second diagram, $\delta^{34}S$ values are plotted in the sequence: atmosphere, tree and ground lichens, leaves, and shallow to deep soil horizons. Low, intermediate, and high impact situations are differentiated on these diagrams. One study was found to be inconsistent with these generalized syntheses. In that case, it was concluded that redistribution of subsurface salts by groundwater significantly influenced the ecosystem.

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1. INTRODUCTION

Mass dependent processes in nature alter the isotopic composition of elements. Therefore, isotope abundances reflect the geochemical history of a sample. This in turn means that raw materials utilized in industrial processing are isotopically characterized and isotopic composition measurements can be used to evaluate contributions of compounds of industrial origin to the environment. The success of this technique requires that (i) the industrial emissions differ significantly in isotopic composition from the surroundings and (ii) isotopically selective processes accompanied by loss of compounds containing the element of interest are minimal in the systems under investigation.

Since the element sulphur exists in many chemical forms and valence states in nature, various processes alter its isotopic composition. It is highly probable that industrial sulphurous emissions will differ isotopically from the surroundings. Further, the processes of oxidizing SO_2 to sulphate in the atmosphere or soil are not accompanied by large sulphur isotope selectivities. As a result, sulphur isotope data have proved effective in tracing the fate of industrial sulphurous emissions in environments throughout the world. These studies have been particularly successful in Alberta.

2. SULPHUR ISOTOPE VARIATIONS IN NATURE: POTENTIAL APPLICATIONS IN ENVIRONMENTAL ASSESSMENT IN ALBERTA

Variations in sulphur abundances are expressed using a ^{34}S scale defined as

$$\delta^{34}S \text{ in } {}^{o}/oo = \left(\frac{(^{34}S/^{32}S) \text{ sample}}{(^{34}S/^{32}S) \text{ standard}} - 1 \right) \times 10^3$$

$^{o}/oo$ is parts per thousand (per mil).

where($^{34}S/^{32}S$) refers to the relative numbers of the two isotopes in the unknown or standard. The standard that is used in laboratories throughout the world, is meteoritic troilite (FeS).

Fig. 1 shows the variations in the $\delta^{34}S$ value which one encounters in nature. Meteoritic troilite has been chosen as the standard because of its isotopic consistency. In comparison to meteorites, today's ocean is 20 parts per thousand (2%) enriched in ^{34}S.

Of particular interest is the variation in hydrogen sulphide in gas wells of Alberta which ranges from about +5 to over +35 per mil. The isotopic composition varies with depth as shown in Fig. 2. This is interpreted as reflecting biological processes in shallow environments, whereas in deeper strata, the H_2S is generated by thermochemical reaction of evaporites (Krouse 1977a). Th deep occurrences which are very enriched in ^{34}S, coincide with very high concentrations of hydrogen sulphide.

When H_2S concentrations are low, it may be simply flared during gas refining. Gases of higher H_2S content are refined by the Claus process and marketable elemental sulphur is a by-product. In either process, SO_2 is emitted from stacks. A basic environmental problem is to determine the fate of these SO_2 emissions in the Province of Alberta. Traditionally, researchers have tended to combine concentration measurements in the atmosphere, hydrosphere, pedosphere, and biosphere with meteorological data. This approach can be used to identify sources of pollutants but it is cumbersome if meteorological parameters vary radically.

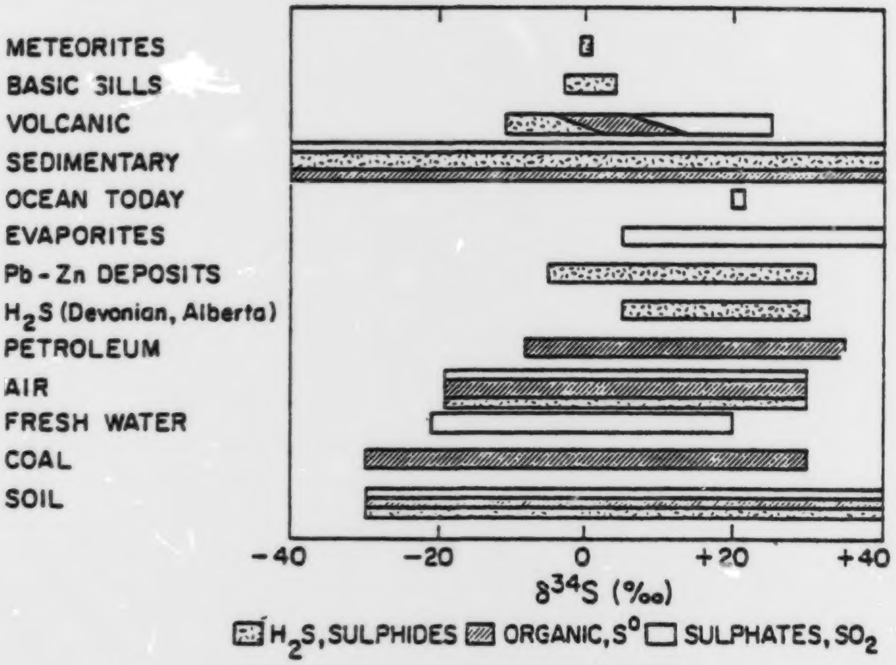


Figure 1. $\delta^{34}S$ variations in Alberta.

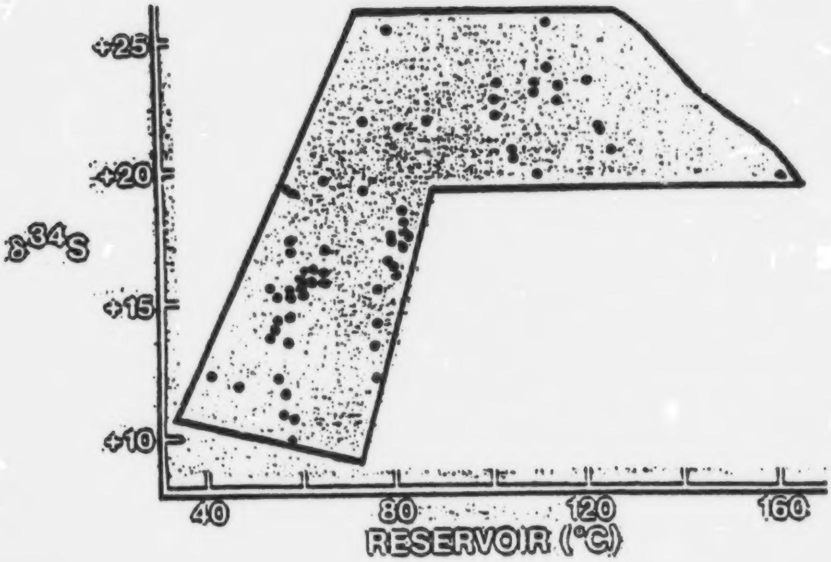


Figure 2. $\delta^{34}S$ variations of H_2S in Devonian Strata of Alberta.

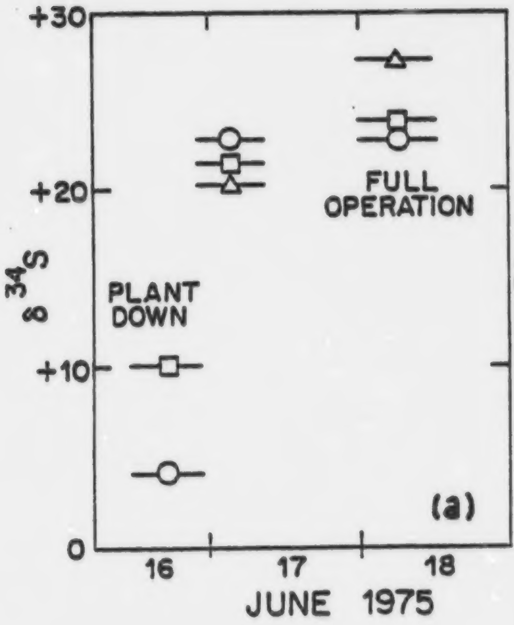
Different sources of sulphur compounds can be identified if they differ markedly in their sulphur isotope composition. It is fortunate that the SO_2 from the sour gas processing industry is enriched in ^{34}S whereas the pre-industrial environment in central and southern Alberta had $\delta^{34}S$ values close to zero. Soil and vegetation in the northwest region, where there is considerable Cretaceous outcropping may have $\delta^{34}S$ values as low as -30 per mil. (Lowe et al. 1971). Thus considerable "isotopic leverage" exists for studying the uptake of the industrial sulphur by the environment.

3. PAST APPLICATIONS OF SULPHUR ISOTOPES TO ENVIRONMENTAL STUDIES IN ALBERTA

3.1 ATMOSPHERIC STUDIES

Contributions of sulphur oxides to the atmosphere in Alberta from sour gas processing are readily discernable using sulphur isotopes. In Fig. 3, the shut down and return to full operation of the gas plant at Crossfield, Alberta was documented by isotopically monitoring the SO_2 at ground level. It can be shown mathematically that if there is a fixed source with a given isotopic composition and an additional variable source with another isotopic composition, a plot of $\delta^{34}S$ versus the reciprocal of concentration gives an intercept corresponding to the $\delta^{34}S$ value of the variable emitter; in this case the industrial plume (Krouse 1980). This procedure shows that the industrial plume had a $\delta^{34}S$ value of +29 per mil. By flying a helicopter with a high volume sampler through the plume, its predicted $\delta^{34}S$ was experimentally verified.

The data at Crossfield were taken over a relatively short time and reasonably constant meteorological conditions. Generally when the wind is blowing from many directions, the pattern takes the form shown in Figure 4. As low concentrations, many individual sources contribute SO_2 at a given site, dependent upon wind direction. When there is a dominant source such as a gas processing plant, the δ values tend to converge to that of the dominant source with increase in concentration. If a histogram is drawn independent of concetration, the most frequently encountered value is also the same as the industrial emitter (Fig. 4).



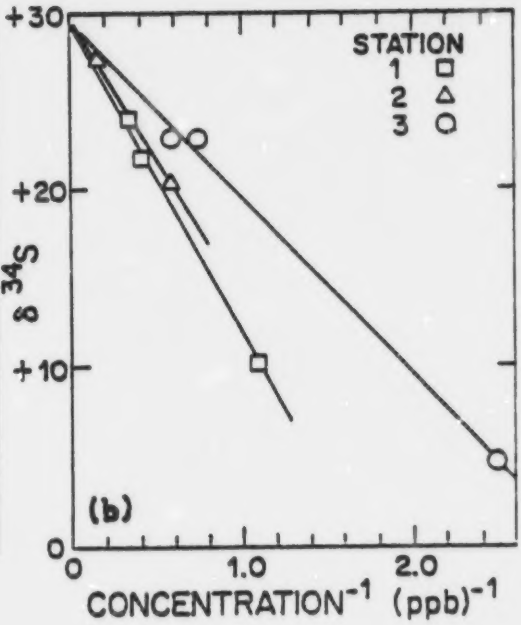


Figure 3a. Variation in $\delta^{34}S$ values of ground level atmospheric SO_2 near Crossfield Alberta during gas plant start up.

Figure 3b. Plot of $\delta^{34}S$ values versus concentration^{-1} assigns a $\delta^{34}S$ value near +29 per mil to the emissions.

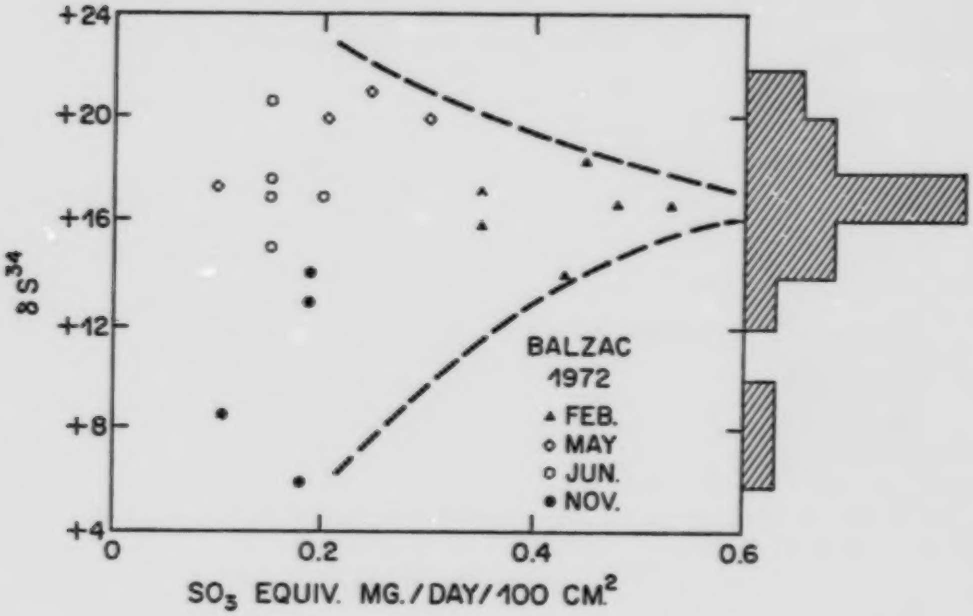


Figure 4. $\delta^{34}S$ data for ground level SO_2 near the gas processing plant at Balzac, Alberta.

The effect of winds from different directions bearing sulphur from different sources to a sampling site is illustrated by a study at West Whitecourt, Alberta (Fig. 5). The sour gas processing plant is off to the northwest and SO_2 from that direction is highly enriched in ^{34}S. As the winds swing from the east, much lower $\delta^{34}S$ values result and as the winds swing back towards the west, $\delta^{34}S$ values increase.

These data were taken with one high volume sampler and were the consequence of an unusual meteorological event (Krouse et al. 1982). For more efficient study of the dependence of wind direction, a high volume sampling array has been constructed which responds to eight different wind directions. It is mounted on a trailer and a ninth sampler is activated if the wind velocity falls below a preset threshold value.

3.2 THE HYDROSPHERE

Using sulphur isotope abundances, sources of pollutants can also be identified in the hydrosphere. Such measurements may be complicated by laminar flows in streams and microbiological conversions in anaerobic environments. This topic is too involved to be included in this brief synthesis. However, an interesting example showing "cause and effect" is illustrated in Fig. 6 where the $\delta^{34}S$ value of sulfate ion in surface waters is plotted against the dissolved organic sulphur content. There is a correlation; the $\delta^{34}S$ values increase with the organic sulphur content, approaching that associated with the nearby industrial emissions (Krouse et al. 1982). The two parameters correlate because the industry emits sulphur enriched in ^{34}S and this sulphur reacts in the environment to form organic sulphur compounds. An occasional anomalous point (asterisks in Fig. 6) arises if there are contributions from elemental sulphur storage blocks.

3.3 VEGETATION

An important question is the extent that sulphur isotopes can be used to assess the uptake of acid emissions by vegetation. Fig. 7 shows earlier data where it was concluded that lichens

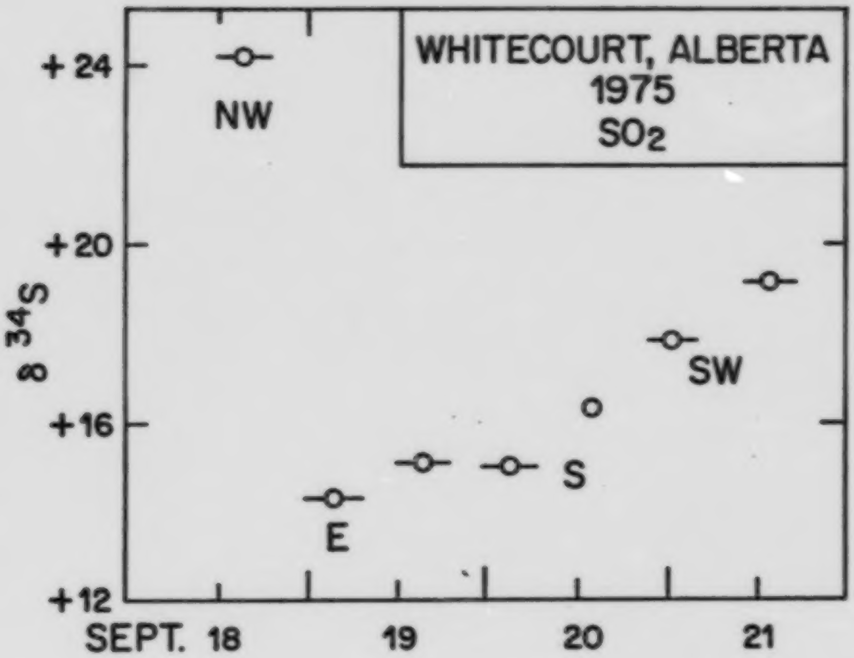


Figure 5. Influence of wind direction on $\delta^{34}S$ values of SO_2 sampled 20 m above ground near Whitecourt, Alberta. the Gas Plant is located to the northwest.

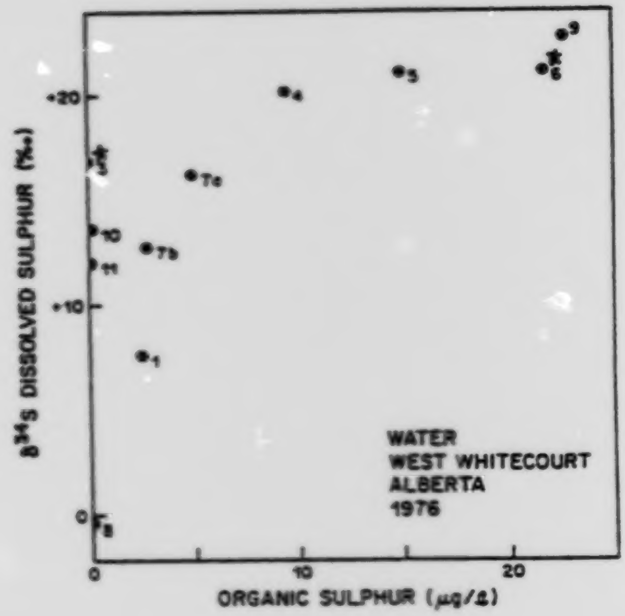


Figure 6. Correlation between δ^{34}S values of SO_4^{2-} and concentration of soluble organic compounds in surface waters near Whitecourt, Alberta, 1975. (Krouse et al. 1982).

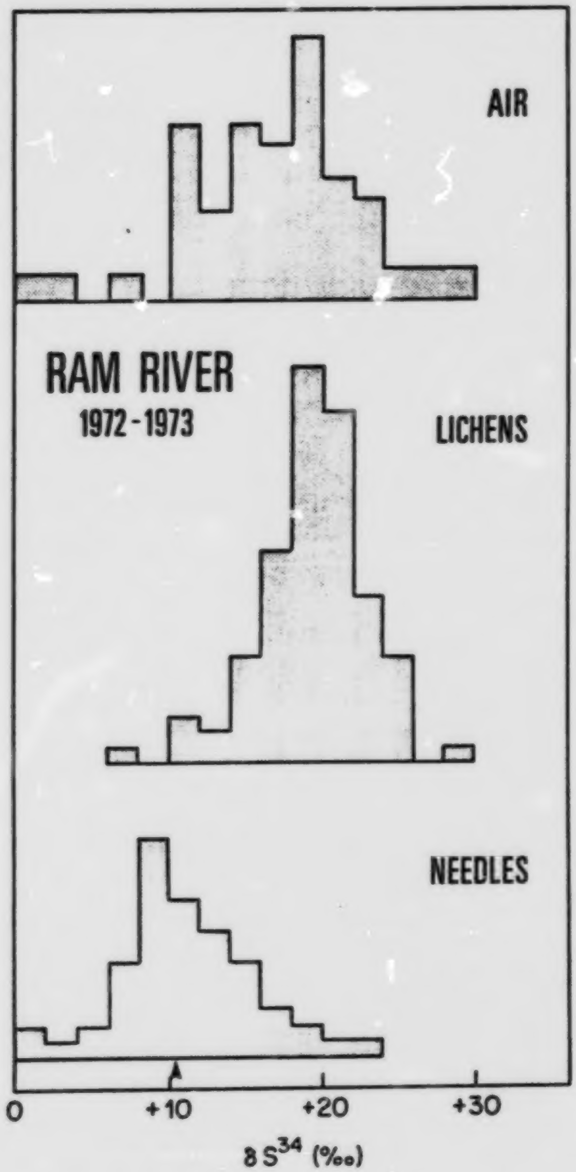


Figure 7. $\delta^{34}S$ data from Ram River. Alberta suggested that lichens acquired atmospheric sulphur by direct means while needles obtained sulphur from both the atmosphere and the soil.

acquired sulphur from the atmosphere by fairly direct means such as chemical reaction with SO_2 or rain-out of sulphate (Krouse 1977b). Since trees have root systems, needles and leaves can derive their sulphur from two sources, namely soluble sulphur compounds in the soil and in the air. In the case of the Ram River study, the soil had $\delta^{34}S$ values around +2 per mil. Thus approximately half of the sulphur in leaves was derived from the soil, and half from the air dependent upon the location relevant to the sour gas plant. Further data from this area are shown in Fig. 8. The control site is sheltered and upwind of the industrial plants and the $\delta^{34}S$ values of the needles are close to that of the soil. At sites around the sour gas processing plants, the $\delta^{34}S$ values are elevated.

3.4 SOIL

The isotopic composition of the soil should also be related to its exposure to the industrial emissions. In the case of the Ram River area in 1974, biological cover entrapped sulphur of industrial origin as shown in Fig. 9. A few centimetres below the surface, the soil retained its pre-industrial value. Generally the amount of industrial sulphur in the soil is dependent upon how long the industry has been operational, the sparsity of biological cover, and the hydrology of the area (Krouse 1980).

Penetration of industrial sulphur compounds into soil can be established by isotopic analyses of soil cores to greater depths than shown in Fig. 9. Examples of deeper isotopic profiles near a gas processing plant at Valleyview, Alberta are shown as a function of distance from the flare stack in Fig. 10 (Krouse and Case 1982). At sites close to the stack, there is a considerable penetration of the industrial sulphur. Although $\delta^{34}S$ values for the total profile have not been elevated to that of the emissions (+20 per mil), high values are encountered in the shallow horizons. In deeper horizons at sites close to the stack, the $\delta^{34}S$ value has been elevated from near -10 per mil up to a value slightly higher than zero. At site 15, there was considerable visual evidence of damage to vascular vegetation while epiphytic and ground lichens had been irradicated. In this study, flaring operations had been ongoing for twenty-four years.

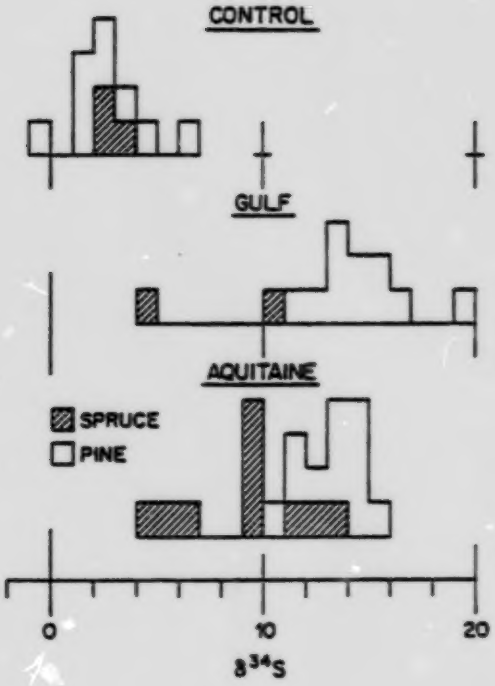


Figure 8. Comparison of $\delta^{34}S$ values of needles influenced by sour gas emissions to those in a control area. Ram River, Alberta, 1974.

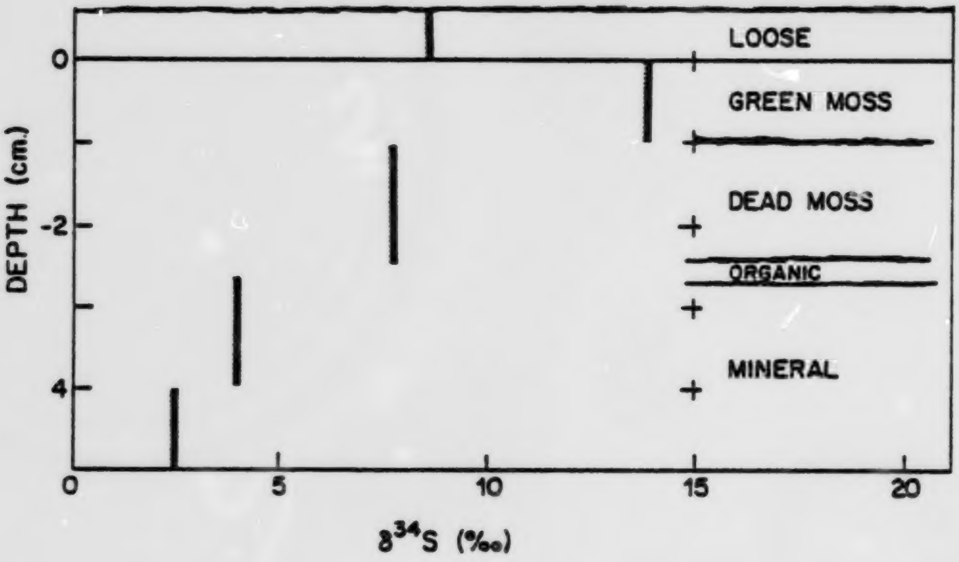


Figure 9. Biological cover entrapment of industrial sulphur demonstrated by sulphur isotope abundances. Ram River, 1974.

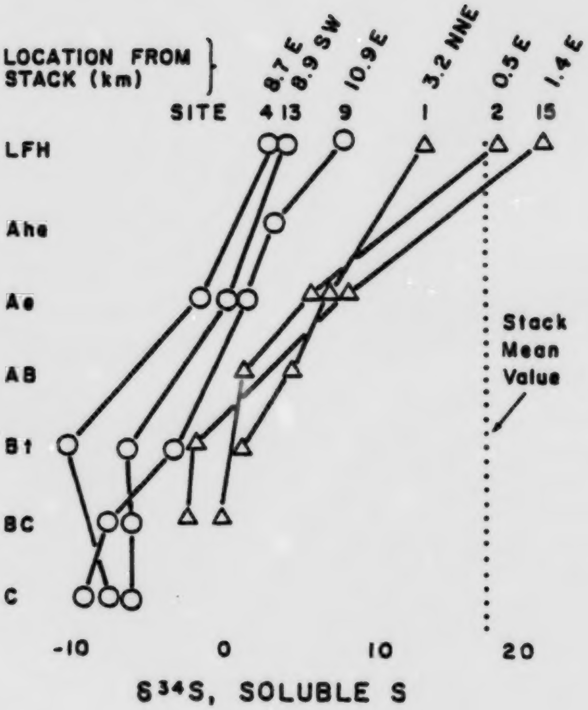


Figure 10. Sulphur isotopic profiles of soil cores at various distances from a source of SO_2 emissions near Valleyview, Alberta, 1981.

In the Teepee Creek area of Alberta, another study was conducted where there was a significant sulphur problem in th soil. There, however, with increasing sulphur concentration, the $\delta^{34}S$ value did not tend towards that of the nearby industry (25 per mil) but rather to very negative values (Fig. 11).

In the Teepee Creek area, the industry had been operating for a very short time. Consequently, when the $\delta^{34}S$ values of leaves are plotted against those for soil horizons, one finds that the points fall more or less about the line of unity slope (Figure 12). This line would correspond to sulphur being derived solely from the soil with no attending isotopic selectivity. In this plot, it would seem that most of the sulphur in the leaves of the aspen was derived from the second uppermost Ae layer. In environments with low atmospheric levels of sulphur compounds, one may argue conversely that sulphur in the soil was derived from litter due to the leaves.

4. COMPOSITE ISOTOPIC DIAGRAMS FOR EVALUATING ACCUMULATIONS OF SULPHUR OF INDUSTRIAL ORIGIN IN THE ENVIRONMENT

The sulphur isotope data from Teepee Creek, Ram River, and the Whitecourt area can be synthesized into composite diagrams. An example is shown in Fig. 13 where the area is not industrially disturbed, the $\delta^{34}S$ values of the leaves plotted against the $\delta^{34}S$ values of the soil fall on the line of unity slope due to the fact that the leaves derive sulphur from the soil, and in turn decaying leaves supply sulphur to the soil. These values fall near 0 per mil and lower. This simplified interpretation neglects transformations of different sulphur compounds in the soil. In the intermediate situation, the soil is still isotopically lighter than atmospheric sulphur compounds. The leaves contain isotopic mixtures of sulphur from the soil and air so these data fall above the line of unity slope.

Where industrial sulphur compounds have penetrated the soil, the situation is similar to the undisturbed soil in that now the soil, atmosphere, and leaves have similar isotopic compositions. However, while the points fall on the line of unity slope, the $\delta^{34}S$ values are higher because of saturation of the environment by the industry. Therefore points falling on the line of slope unity in Fig. 13, may

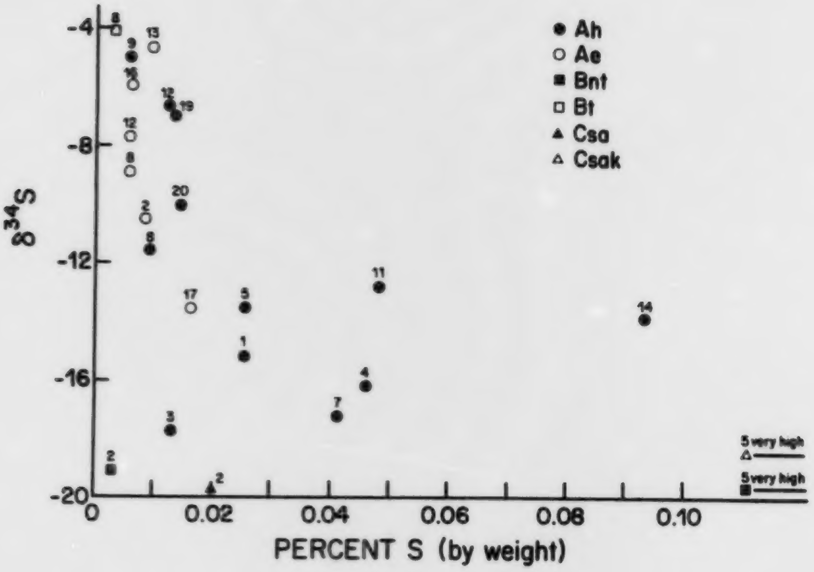


Figure 11. At Teepee Creek, Alberta, sulphur isotope data revealed that increased soil sulphur content was identified with subsurface salt layers (Krouse and Case 1981).

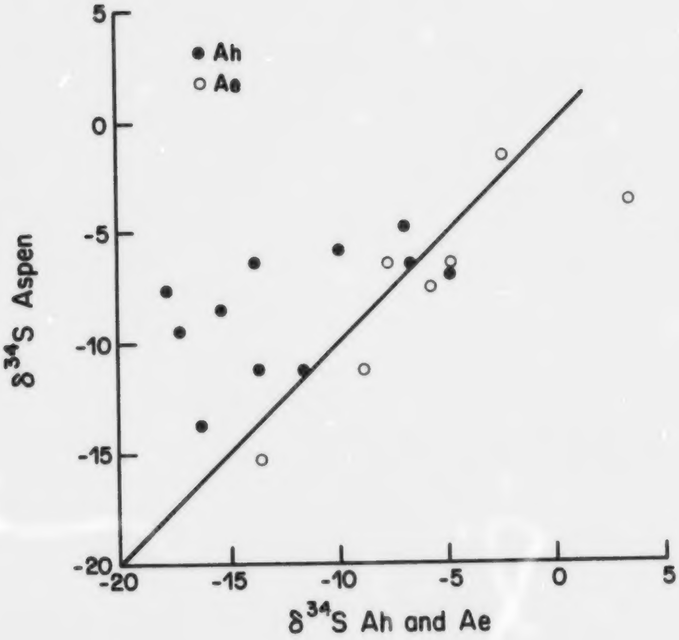


Figure 12. $\delta^{34}S$ values of Aspen leaves versus same for soil sulphur show that the foliar sulphur is derived from the Ae horizon (Krouse and Case 1981).

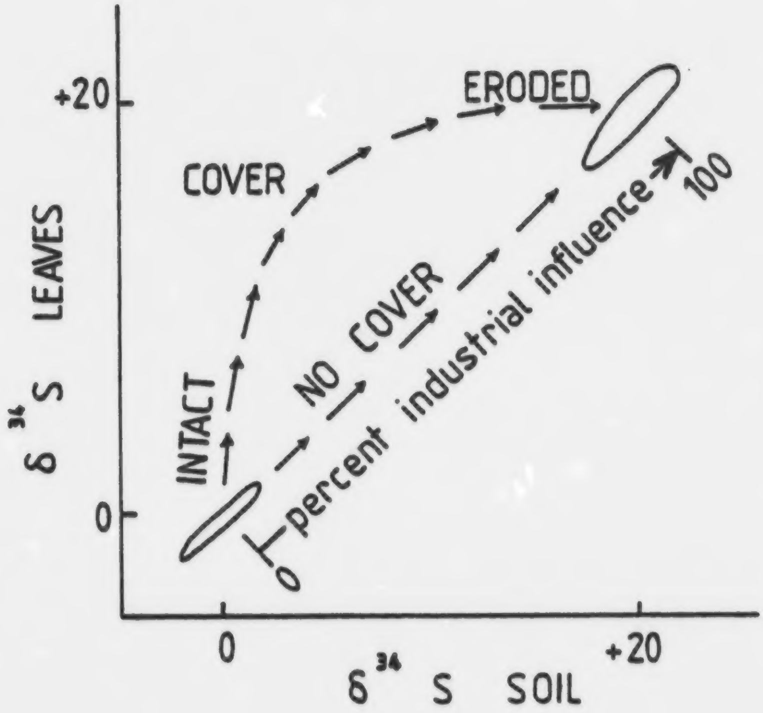

+20
0
$\delta^{34}S$ LEAVES
COVER
ERODED
INTACT
NO COVER
percent industrial influence
0
100
0
+20
$\delta^{34}S$ SOIL

Figure 13. $\delta^{34}S$ values of leaves versus the same for soil as a function of exposure to industrial emissions.

represent either undisturbed situations or the environments dominated by industrial sulphur. For locations where emissions are isotopically lighter than the pre-industrial environment, points for intermediate situations would fall below the line on this diagram.

In preliminary studies in the Ram River area, it was concluded that lichens acquired a sulphur isotopic composition similar to the air. Those particular lichens were epiphytic and this generalization cannot be extended to all types of lichens and mosses. In particular, species dwelling near the ground appear to acquire some sulphur from the litter layer and tend to have $\delta^{34}S$ values between the epiphytic lichens and leaves. These observations suggest another synthesis of isotopic data (Fig. 14).

This synthesis examines the $\delta^{34}S$ values from the deep soil profiles upwards to epiphytic lichens. Assuming that the pre-industrial $\delta^{34}S$ value of the environment was near zero, all soil layers and species presumably had values around zero. Going to the intermediate situation, there is some penetration of ^{34}S enriched industrial sulphur compounds into soil layers. The concentrations of these compounds and hence the $\delta^{34}S$ value decrease with depth. The sulphur isotopic composition of atmospheric compounds is slightly less than that of the industrial emitter because of minor natural sources. Epiphytic lichens have $\delta^{34}S$ values close to that of the atmosphere; $\delta^{34}S$ values of trees fall intermediately between the soil and the atmosphere and usually display a height trend with the uppermost needles possessing a higher component of atmospheric sulphur than the lower ones. This presumably relates to a canopy action which the upper needles exert. The ground lichens and mosses have $\delta^{34}S$ values between those of the trees and epiphytic lichens. In the highly polluted situation where atmospheric sulphur compounds have $\delta^{34}S$ values near +20 per mil, the trees and epiphytic lichens may be +20 per mil or slightly higher. The reason for values slightly higher than the ambient SO_2 relates to re-emission of sulphur compounds by the vegetation. This process has been found to be isotopically selective in studies where photo enhanced release of hydrogen sulfide from cucumber leaves was accompanied by the hydrogen sulfide being depleted in ^{34}S (Winner et al. 1981). Hence, sulphur remaining in the vascular tissues was enriched in ^{34}S. This enrichment occurs at very

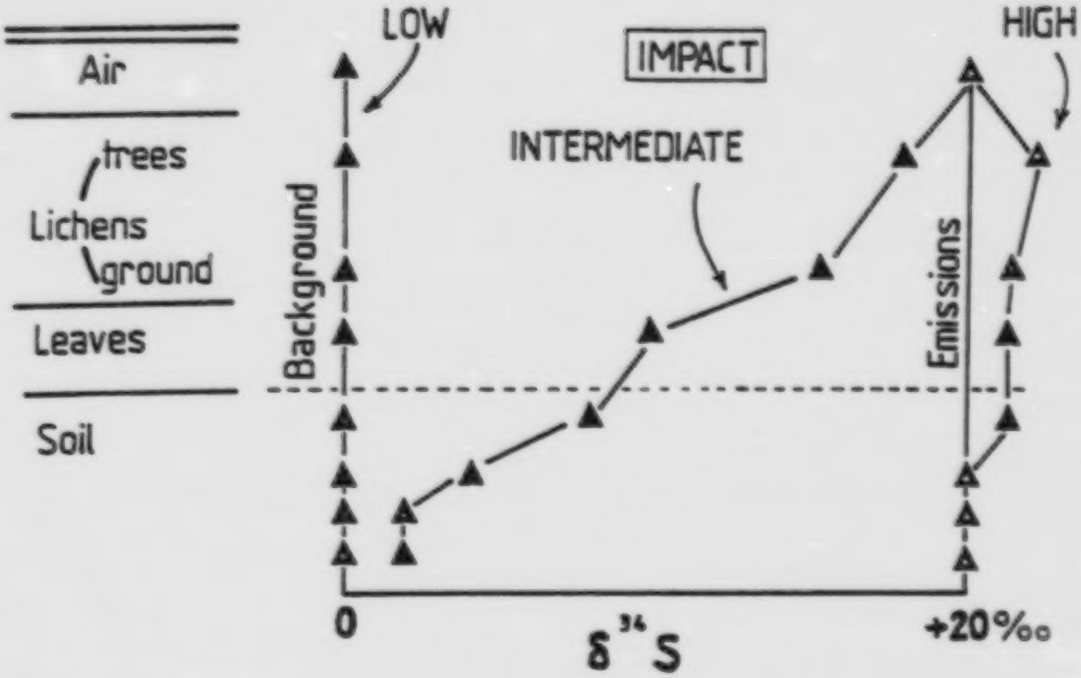

Air
trees
Lichens
ground
Leaves
Soil
LOW
IMPACT
HIGH
INTERMEDIATE
Background
Emissions
0
+20‰
$\delta^{34}S$

Figure 14. Generalized behaviour of $\delta^{34}S$ values for components in ecosystems in Alberta as a function of exposure to industrial sulphurous emissions.

high sulphur concentrations and is in itself an indicator of very severe stress due to uptake of sulphur compounds.

5. DEPARTURES FROM THE COMPOSITE ISOTOPIC DIAGRAMS: THE ZAMA STUDY

While the syntheses of Figures 14 and 15 generally apply, situations were encountered where the interpretation was not straightforward. Such was the case in the Zama area of Alberta. Higher foliar $\delta^{34}S$ values were not consistent with either higher sulphur content or evidence of damage. It turned out however that the foliar $\delta^{34}S$ values displayed an elevation dependence (Fig. 15) with lower $\delta^{34}S$ values and usually higher sulphur concentrations found at lower elevations.

The data were interpreted in terms of accumulations of subsurface salts with negative $\delta^{34}S$ values in depressions. Trees growing in these depressions would acquire much sulphur from the soil. In this situation, small amounts of sulphur acquired from industrial emissions could have a marked impact, but the $\delta^{34}S$ value would not be significantly changed. In contrast, trees at higher elevations acquired little sulphur from the soil in comparison to uptake from the atmosphere. The foliar $\delta^{34}S$ values would therefore be close to those of the gas plant emissions. If the sulphur derived from both sources was not excessive, the trees would be quite healthy.

6. CONCLUDING REMARKS

In conclusion, it is important to emphasize the role that sulphur isotopes play in assessing the impact of sulphurous emissions on the environment. They document the presence of sulphur of industrial origin without ambiguities which may arise with other techniques (i.e., they show that a suspect was present on the scene but they do not characterize any crime). They identify a possible cause but in very few cases relate "cause" to "effect" as shown in Figure 6.

Despite a decade of sulphur isotope studies in environmental assessment in Alberta, there are still many unexplored research avenues. Isotopic investigations of individual or groups of sulphur

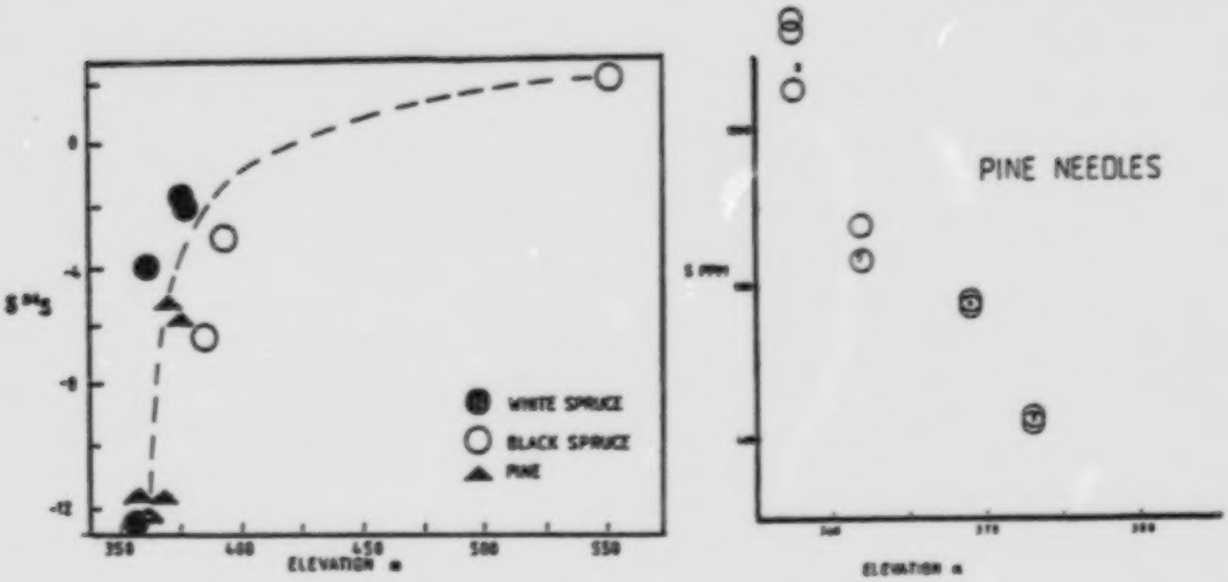


Figure 15. $\delta^{34}S$ values of foliar sulphur in the Zama area displayed an elevation dependence but were not simply related to either sulphur content or vegetation damage.

compounds should receive more emphasis. These should further elucidate transformations of sulphur compounds in the environment and perhaps serve to better relate cause to effect. Measuring other chemical and biological parameters more consistently with sulphur isotope abundances should also establish better cause and effect relationships.

The success of the sulphur isotope investigations suggest that similar programmes should be considered for other elements. In connection with acid emissions, nitrogen is an obvious candidate for preliminary studies to see if suitable isotopic leverage exists.

ACKNOWLEDGEMENTS

Since this paper is a synthesis based on a decade of measurements, a chronological sequence of support is appropriate. Initially, ^{34}S enrichments in atmospheric sulphur compounds were found in samples supplied by Alberta Environment. The first investigation of vegetation was carried out in the Ram River area with financial assistance from Aquitaine Ltd. This work demonstrated that foliar sulphur was derived from both the air and ground. Further studies on vegetation were supported by the Canadian Forestry Service. As the result of a National Research Council Negotiated Development Grant, the University of Calgary Interdisciplinary Sulphur Research Group (UNISUL) was established and the methodology further developed. Measurement capabilities were enhanced and effective interaction with the major project of the West Whitecourt Study Group occurred. In recent years, major investigations have been funded by Alberta Environment and smaller projects by resource companies including Gulf, Hudson's Bay Oil and Gas, and Esso Resources. Thus federal and provincial agencies and the private sector have all financially supported these studies. The success also depended in no small way upon interactions over the years with numerous individuals which are acknowledged collectively rather than listed individually.

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TRANSPORT AND POTENTIAL EFFECTS OF ACIDIC DEPOSITION IN NORTHEASTERN ALBERTA AND NORTHERN SASKATCHEWAN: A PROBLEM ANALYSIS

S.R. Shewchuk[1], J. Maybank[1]

Abstract

This is a review paper which deals with the main conclusions and recommendations of a recently completed study dealing with acidic deposition within a selected area of northeastern Alberta and northern Saskatchewan. Emissions of both sulphur and nitrogen oxides were considered within the area. Possible acid depositions were addressed. The geology, soils, natural vegetation, and aquatic systems were described with particular reference to their response to acidic depositions.

An area termed the Precambrian Shield was identified as being highly sensitive to acidic deposition. In particular, aquatic systems within this structure are the likely locations where first effects would be identified.

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1. INTRODUCTION

Following production and emission by natural anthropogenic sources, sulphur and nitrogen gases are carried great distances in the air, and tend to become oxidized to sulphuric and nitric acids, in which forms they are readily incorporated into raindrops or snow-crystals. Precipitation, which usually starts off in the cloud in a slightly acid state already, is rendered more acidic as it falls. In addition, these sulphur and nitrogen compounds fall out directly on the ground, or else can be absorbed by vegetation in the absence of precipitation; these dry deposition processes also contribute to the overall loading of the lakes, soil and vegetation of any region.

Problems arise when additional emissions of SO_2 or NO_x occur upwind of relatively sensitive ecosystems that cannot assimilate the resulting increase in deposition. Human activity has introduced many new sources for both SO_2 and NO_x. Anthropogenic emissions of SO_2 have been growing steadily over the past decades to roughly 70% of the natural emission level; major sources are coal and oil combustion processes and smelting. The combination of sensitive areas in proximity to significant anthropogenic sources is naturally of concern. The purpose of this presentation is to show the relative susceptibility of these northern areas in both Alberta and Saskatchewan.

2. EMISSIONS, AIR FLOWS AND DEPOSITIONS

The emissions, transport and deposition of acids to ecosystems of northeastern Alberta and northern Saskatchewan have been outlined in Shewchuk et al 1981. Main industrial emissions are centered in the oil sands portion of Alberta and the metal smelting portions near Saskatchewan at Flin Flon.

The general airflow pattern can also be superimposed on either source area to obtain rough indications of what the pollutant trajectories might be. They show that winds capable of carrying emissions from the oil sands over some portion of the Precambrian Shield area, i.e., winds ranging from northwest through to south, occur about 50% of the time, over the course of the year.

A critical requirement is to be able to estimate what fraction of the regionally produced emissions deposits out internally, especially in the Precambrian shield area. Conceivably, it could range from zero (leaving the deposition rate unchanged at the present level), to total deposition (leaving the background air concentration unchanged as it leaves the region). Obviously, the appropriate value lies between these extremes, but great variation must be expected both in space and time.

3. GEOLOGY

The survey of potential pollutant effects on the environment involved four separate investigations: geology, soils, terrestrial vegetation and aquatic systems. These were then integrated to give an overall depiction of relative sensitivity on an areal basis for different portions of the region. The key aspect in each case was the division between the Precambrian Shield and the rest of the region.

The soil and water surface onto which both naturally-produced and anthropogenic sulphates (and nitrates) deposit out is extremely complex. The response of a system to acid input is determined primarily by fundamental acid-base relationships for surface waters and for soil groundwater systems.

As additional acid material deposits onto the surface it reacts with basic ions and thereby re-establishes an equilibrium. The most common source for basic ions in nature is calcium carbonate. The presence of $CaCO_3$ (or other carbonate compounds) is variously referred to as the buffering capability or BFC (for soils) or as the alkalinity (for surface waters). A relatively high concentration in either soil or water is indicative of the ability to neutralize and assimilate some further influx of sulphuric or nitric acid. Low or negligible levels and the absence of sources from which carbonates might be dissolved, depicts soil or water bodies that are sensitive to such influx and would be altered thereby.

The bedrock and associated drift material overlying it are obvious potential sources of buffering material. As found from the geological survey of the area the availability of carbonaceous (carbonate-containing) material varies widely, being low throughout the Precambrian Shield. Rock material in this area consists primarily of two types, viz. sandstone and so-called "basement" rocks. The former overlies the latter throughout the north-central portion of the region, and is practically devoid of buffering capability. Surrounding it, the basement rocks consist mostly of granite or related impermeable forms. However, there is an amount of mafic and clay material overlying and intermingled with the granite; hence, the overall geology of this part of the Precambrian possesses some small capacity for assimilating sulphates.

Cretaceous rocks underly most of the high plains area. These consist of shales and sandstones primarily, interbedded with varying amounts of carbonaceous sedimentary rocks. Unlike the Precambrian Shield, the bedrock here is nearly entirely covered with thick clay and carbonate-rich drift. The relative availability of buffering material results in the portion of the region being considered is of intermediate to low sensitivity with respect to further acid deposition.

Finally, lying as an intermittent zone between the two main geologic features, is a belt of silurian and devonian rocks. These are mainly limestones and dolomites, and as such are rich in easily dissolved carbonate material. This belt can be considered to have definitely low sensitivity to acid influx. By its relatively narrow nature, it serves more to sharpen the distinction between the highly sensitive Precambrian to the north and east and the less sensitive areas to the south and west than to qualify as an area completely separate from the latter.

4. SOILS

Soil surveys have been undertaken for a variety of purposes throughout most of the region (although a sizeable area in Saskatchewan has been missed). Properties relevant to buffering capability and the resulting sensitivity to acid deposition vary greatly, and quite diverse soil types are frequently intermingled. Nevertheless, a pattern can be discerned that is compatible with the underlying geological features.

Present analyses indicate that most soils in the Precambrian portions are already quite acidic, due to natural causes such as organic decomposition processes in bogs and muskegs. Those in the Interior Plains areas range from acidic (for the same reasons) to alkaline, this latter condition being typical of the agricultural soils over much of southern Alberta and Saskatchewan. Once again, however, it is not the present pH level but the presence of buffering ions that govern sensitivity or resistance to change.

Overlying the Athabasca sandstone formation are thin acidic soils with little buffering capability. They are sandy and highly permeable, so that acid-bearing precipitation would rapidly penetrate, further diminishing the already low base ion content but tending to be relatively unaltered itself during passage. It would therefore enter streams and lakes with essentially the same pH value as it possessed on reaching the surface. The soils, already quite acid, would exhibit only minimal change in their own pH figures.

Soils overlying the rest of the Precambrian Shield tend to be almost equally acidic at the present time, with little buffering capability near the surface. However, as they tend to be somewhat thicker and to contain finer, silty material at lower depths, somewhat more buffering action and neutralization can take place for soil water that reaches these depths.

South and west of the Precambrian, the soils tend to be of intermediate sensitivity, although the most common sub-categories through the south-central portion of the region may already be quite acidic. Clay and loam components are significantly higher, together with considerable calcareous ($CaCO_3$ or equivalent) material at lower depths. Permeability for soil water is generally lower than in the Precambrian soils, and the moisture holding capacity higher.

Finally, along the southern and western borders of the region, the soils tend towards alkalinity. Such soils contain considerable organic material, plus a mixture of calcareous substances capable of supplying buffering ions.

5. NATURAL VEGETATION

The literature survey of terrestrial system response to acid input indicates that effects occur via two different translocation routes, and are of two broad types. One route, that of direct acid deposition on foliage has been shown, by controlled experiments in growth chambers, to produce lesions, to interfere with photosynthesis and to affect seed production and germinability. Such damage is generally confined to acidities below pH 4. More difficult to identify, and to establish threshold levels for, are indirect or soil-mediated effects resulting from acid deposition on the soil leaching away plant nutrients. Higher plants are generally fairly tolerant of intermittently elevated acidity levels provided nutrients remain available within reach of their root systems. Lichens, which depend on the rain for much of their nutrient intake, are considerably more sensitive.

As might be expected, terrestrial biota sensitivity to direct effects will be essentially a function of distance downwind from strong sources, while sensitivity to indirect effects will be closely related to the soil sensitivities themselves. From the information presently available, one can reasonably assign a relative sensitivity scale to the various ecological areas within the region of this soil-type basis. However, it is not yet possible to assign an absolute or quantitative sensitivity, which in any case would have to be connected to particular plant species (e.g., lichens, conifers, etc.) and to their distribution.

6. AQUATIC SYSTEMS

It is generally accepted that lakes and the biota that reside in them represent a more sensitive overall system to acid rain effects than does the terrestrial domain. Recently, completed surveys of small lakes in northern Saskatchewan and parts of Alberta have provided much valuable insight into present conditions. Most lakes within the region are currently close to neutral, with pH's ranging from 6.5 to 7.5. Lakes more acidic than 6.5 do occur, the result primarily of natural acid-bog conditions. Sulphate content in northern Saskatchewan lakes is less than 2 mg ($SO_4^=$)/litre, which is typical of a lake not yet affected by acid rain. In particular, the alkalinities of the Precambrian Shield lakes are highly correlated with the associated concentrations of calcium and magnesium ions. Such a correlation is further evidence that the natural alkalinity in these systems is not yet being consumed by anthropogenic acid processes.

As with the soils, it is this alkalinity factor that determines a lake's ability to handle any increase in annual acid deposition from the atmosphere. Once again, the ability to neutralize such acid input and thereby buffer the water, can be related to the concentration of calcareous material dissolved in it. Present criteria designate as "highly sensitive" those lakes containing less than 10 mg/litre of $CaCO_3$, with ones containing 10 to 20 mg/litre being characterized as "moderately sensitive". "Least sensitive to insensitive" is used to describe lakes within the broad ranges of $CaCO_3$ concentration of 21 to 40 and more than 40 mg/litre.

Adjacent lakes may vary considerably in their alkalinity content, due mainly to the relative availability of replacement carbonates in lake bottom sediments or along the beds of inflowing streams. Nevertheless, the survey to date has indicated that more than 70% of the lakes within the Precambrian Shield are highly to moderately sensitive, with many having extremely low $CaCO_3$ concentrations. Outside this area, most lakes are moderately to well-buffered, although exceptions have been found.

It is possible in principle to estimate the response of a lake to increased acid deposition, and to gauge the rate at which its pH might be reduced, by treating the system as a large scale acid-base titration. A doubling of the present sulphate deposition rate into a lake 5 metres deep with only 5 mg ($CaCO_3$)/litre alkalinity would reduce its pH from 7 to 5.5 within 20 years, assuming the lake had no capability of replacing its loss of carbonate material. Such replacement processes would limit the pH drop but could not prevent some reduction over this time period. On the other hand, lakes containing 20 or more mg/litre of $CaCO_3$ would appear to be impervious to damage unless sulphate emissions reached a level such as to produce consistent acid precipitation values below a pH of 4.

Evidence from other areas suggests that acidification effects may begin to be observed once the pH of a lake drops below 6.5, and can be both serious and extensive if the pH drops below 6.0. Fish populations dwindle and some species disappear; lake trout and walleye are among the more sensitive and can possibly serve as indicators of incipient problems. Small muskeg lakes in the region, already acidified by various naturally-produced humic acids, exhibit some features in common with anthropogenic sulphate acidification; they may detrimentally influence nearby sensitive lakes by reducing their already low buffering capabilities.

One other feature of concern for the welfare of aquatic life in even well-buffered lakes is the occurrence of an "acid shock" in spring, brought about by the rapid melting of the snow pack covering the lake's drainage basin. Quite low pH values are commonly observed in such meltwater, if wet and dry sulphate deposition has been high over the winter, as the snow tends to lack buffering capability. This water enters the lake via the local streams and while the high acid level is a transient phenomenon it can have very serious implications for those fish species that customarily spawn in the streams at that time of year.

7. CONCLUSIONS

Much of the region must be described as sensitive to acidification, with the most sensitive area being the Athabasca Sandstone portion of the Precambrian Shield. In particular, alkalinity levels for many of the lakes in this area are very much lower than worldwide averages, and in some cases are close to the lowest values found anywhere. Such lakes have essentially no capability to assimilate increased sulphur loading, and very preliminary estimates suggest that serious damage will ensure should deposition double over the present value of 4 kg $(S)/ha \cdot yr^{-1}$. Furthermore, as the Athabasca Sandstone location puts it down the general westerly-to-easterly track of prevailing winds from the major SO_2 source within the region, the area must be considered susceptible to future damage, particularly as emission rates there appear likely to significantly rise by 2010 A.D.

The only viable course of action is to ensure that emission rates do not lead to depositions in excess of the ability of the regional environment to cope with them. It must be obvious that there are presently many uncertain factors, the key one being that it is not yet possible to determine the deposition increases that would result from any given rise in emission rate. The recommendations that follow are designed to help resolve these uncertainties so as to ensure that appropriate and soundly-based guidelines can be established and refined as development proceeds. Fortunately, there appears to be sufficient time to plan, coordinate and undertake a major research program to do this for the region, provided the work is started now and not after damage begins to be suspected.

8. RECOMMENDATIONS

It is recommended that:

1. All new developments planned for the region be analyzed for their probable sulphur and nitrogen emission levels, and that interim emission controls be devised to guide such development from the outset.
2. A detailed SO_2, NO_x and particulate emissions grid be constructed for the region that will include considerations of background and industrial emissions inflows and outflows, and that will provide estimates of incremental emissions levels to be expected at 5-year intervals up to 2010 A.D.
3. Improved station networks including an upper air station at Cree Lake be established to provide greater wind and precipitation data, and that a program of air sampling by aircraft be undertaken to more effectively determine dispersion, pollutant trajectories, precipitation-acidifying processes and deposition rates for the region.
4. An immediate start be made on air, rain and snow sampling via a monitoring network of air pollution stations, precipitation event collectors and snow surveys throughout the region, to establish background levels, identify episode events, provide data on acidification anomalies and to aid in determining the relative roles of dry and wet deposition.

5. A few small lakes be selected on the basis of size and alkalinity as monitoring sites now; that a major small lake inventory survey be undertaken to identify present range and sensitive features. This survey be used as the basis for a subsequent full scale lake monitoring program. Spring snowmelt shock effect should be emphasized in any aquatic program.
6. Appropriate soil inventory and research on geological studies and related laboratory analyses be undertaken to delineate more quantitatively and characterize surface sensitivities to acidic deposition.
7. Relative sensitivity of the important terrestrial and aquatic organisms to acidic precipitation be investigated and that a comprehensive biomonitoring network be planned and established on the basis of the obtained information to detect any acidification effects at the earliest possible stage.
8. Attention be directed toward the selection of small areas, i.e. calibrated watersheds, within the study area, possibly in Cree Lake - La Ronge area of Fort Chipewyan - Lake Athabasca area of Precambrian Shield where an intensive multidisciplinary research program could be mounted on the interactions of geology, soils, vegetation, surface waters, groundwaters, muskeg lakes and atmospheric acid deposition.
9. The study area be enlarged to the entire area of western Canada, thereby including the Precambrian Shield portions of Manitoba and the Northwest Territories for attention.
10. Acidic deposition in the area be evaluated by means of analyzing atmospheric trajectories in the context of known and predicted emissions.

9. REFERENCE

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A STATISTICALLY DERIVED FORECAST SCHEME FOR WINDS AND TEMPERATURES IN THE ATHABASCA TAR SANDS AREA

M.C. HANSEN[1], D.M. LEAHEY[1]

ABSTRACT

A forecast scheme has been developed for predicting 8 hours in advance of real time the observed wind and temperature fields at the Syncrude Canada Ltd. Athabasca Tar Sands extraction plant in northeastern Alberta. Such a scheme could allow for the maintenance of ground level air quality within desirable limits by controlling plant operation and resulting stack emissions according to the forecasted dispersion potential of the local atmosphere.

Multiple linear regression techniques were used to derive forecast relations between site specific wind and temperature predictands obtained from 2289 minisonde and 2399 pibal observations over the years 1975 and 1979 inclusive, and concurrent predictors from national, regional, and local sources of meteorological data.

Approximately half of the 2471 wind and temperature predictand observations were randomly selected to derive forecast equations. Values for the multiple correlation coefficients squared (R^2) for wind and temperature regression equations were about 0.55 and 0.29, respectively. Testing of the equations with the remaining portion of observations gave R^2 values for wind and temperature predictands of about 0.48 and 0.10, respectively.

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1. INTRODUCTION

Syncrude Canada Ltd. operates an oil sands extraction plant located about 50 km north of Fort McMurray (Figure 1). It may emit up to 292 t/d of sulphur dioxide from a 183-m high main stack. This stack is designed so that ground-level air quality will remain within the ambient objectives under most meteorological conditions. During some situations, for example those relating to fumigation, plume trapping, or high winds, concentrations of ground-level sulphur dioxide may exceed the air quality objectives.

To attain a zero exceedance policy, an air quality prediction scheme must be used. Such a scheme would require accurate forecasts of meteorological variables some eight hours in advance of real time in order for required changes in plant procedures to be implemented. Specific meteorological parameters needed for an air quality modelling scheme are: wind speed and direction at plume height, vertical temperature gradient at stack height, mixing layer height, and turbulence levels. Information specific to the oil sands area for these parameters is available from minisonde and pilot balloon data obtained from 1975 to 1979, and from meteorological tower data.

The Canadian Atmospheric Environment Service (AES) issues forecasts of wind and temperature that tend to be regional rather than site specific due to the relative coarse grid spacing associated with their forecast model. For this reason, AES forecasts cannot usually be accurately applied to a specific site. This is true of the Athabasca Oil Sands area near Fort McMurray where terrain effects appreciably influence the wind field. AES forecasts may be adjusted by statistical means to make them more specific to the oil sands area. This may be done by establishing a statistical relationship between forecast model outputs and meteorological parameters measured within the area of Fort McMurray.

Two methods can be used to develop and test statistical relationships between a desired predictand and a number of predictor variables from a numerical model. The difference between the two methods lies in nature of predictor data used in the development phase. One method,

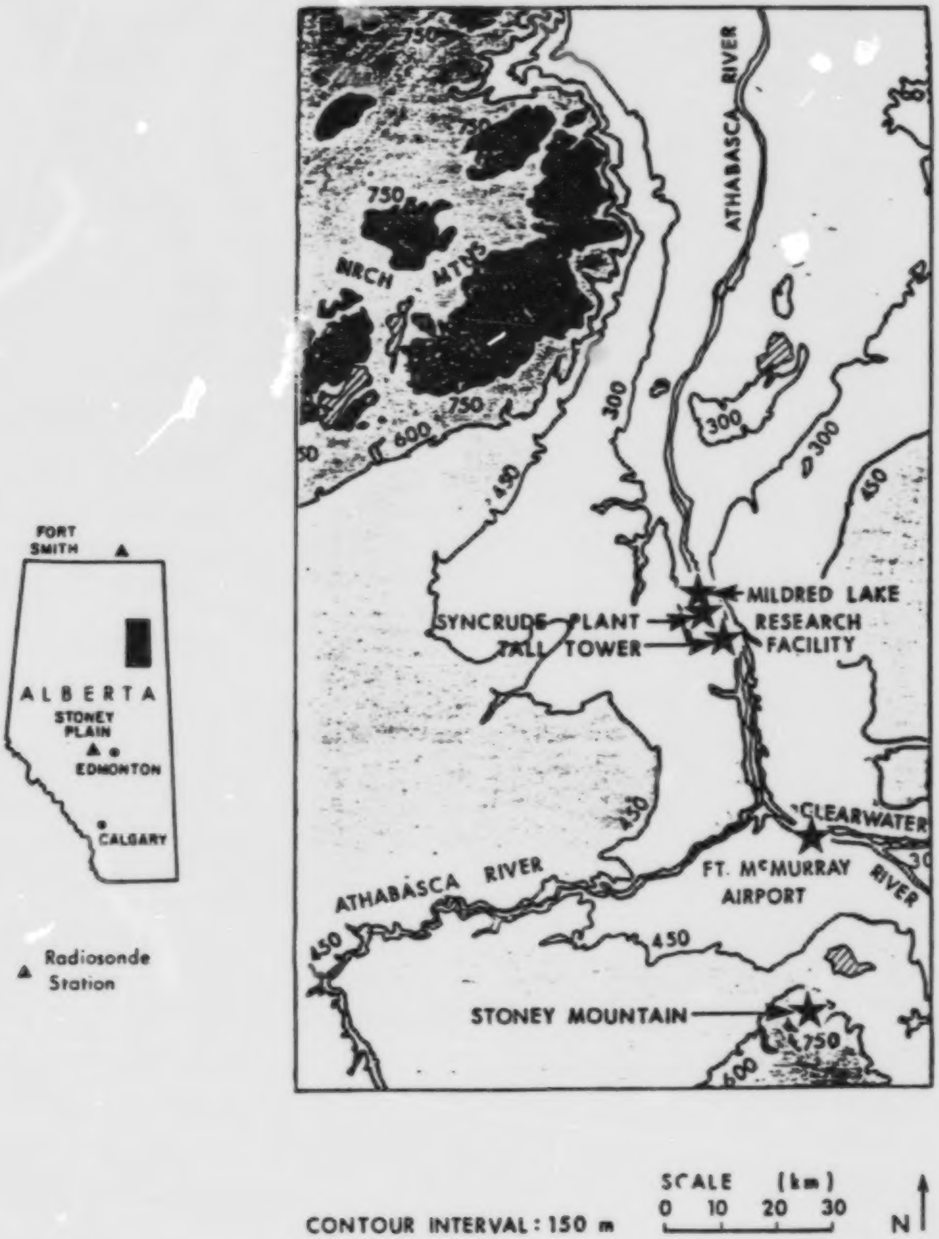
BIRCH MTNS
750
600
450
300
ATHABASCA RIVER
MILDRED LAKE
SYNCRUDE PLANT
TALL TOWER
RESEARCH FACILITY
CLEARWATER RIVER
FT. McMURRAY AIRPORT
STONEY MOUNTAIN
FORT SMITH
ALBERTA
STONEY PLAIN
EDMONTON
CALGARY
Radiosonde Station
CONTOUR INTERVAL: 150 m
SCALE (km)
0 10 20 30
N

Figure 1. Locations of meteorological sites in the vicinity of the Syncrude oil sands plant, and the nearest radiosonde stations.

called model output statistics (MOS), uses as predictors values from a numerical model applicable at a required time. The other method, called the perfect prog method, uses actual observed values at the required time. Both methods utilize predicted numerical model parameters during the forecast phase.

Ideally, the MOS method could be used in developing a forecast scheme between the desired predictand and a number of predictor variables. Unfortunately, predicted meteorological parameters are not available from AES for the period over which minisonde and pibal data from the oil sands region are available. Therefore, the perfect prog method has been adopted for the forecast scheme.

2. THEORY

Multiple linear regression was used to relate one variable, Y, called the dependent variable of predictand, to k other variables, X_i, called the independent variables or predictors. The result is an equation which can be used for estimating the predictand as a linear combination of the predictors:

$$\hat{Y} = A_o + A_1 + X_1 + A_2 X_2 + \ldots\ldots A_k X_k \tag{1}$$

The caret indicates an estimate and the A_i's are the regression constant and coefficients. They are determined such that the sum of the squares of the estimation errors between individual observed and predicted values, Q, is a minimum on the developmental samples of size n. That is:

$$Q = \sum_{j=1}^{n} (y_j - \hat{y}_j)^2 = \text{minimum} \tag{2}$$

There are several methods for screening predictors to include in a regression equation. The one adopted for development of the forecast scheme is called the forward stepwise method. The first step in the procedure is to select the variable which correlates most highly (in either a positive or negative sense) with the predictand. This is the variable which explains a greater fraction of the predictand variance than any other of those available. The next step is to select the variable which, together with the first, reduces the residual variance the most. Selection can continue in this way until some special cutoff criterion is met. Usually, the cutoff criterion is some function of the reduction of residual variance afforded by the next best predicator. A discussion of the screening technique and the necessary matrix operations is given by Efroymson (1960).

3. PREDICTANDS

Some meteorological parameters required for an air quality prediction scheme, specifically the mathematical and physical components, are:

- wind speeds at stack and plume heights,
- wind directions at stack and plume heights,
- vertical temperature gradients at stack height, and
- height of mixing layer.

Forecast schemes for these four predicants were developed using the perfect prog statistical approach.

3.1 WIND AT PLUME HEIGHT

Wind speed and direction may be used to estimate plume rise, determine plume position, indicate turbulence levels of the atmosphere, and, hence, estimate ground level pollutant concentrations. In order to derive predictands relating to wind speed and direction at plume height, it is first necessary to know the plume height. Plume height is the sum of the physical stack height and the plume rise. Plume rise was determined with formulations developed by Briggs (1971, 1975) and Djurfors-Netterville (1978). They are similar, except the Djurfors-Netterville formulations take into account wind speed shears.

Regression of wind direction posed a problem because of the circular nature of the variable. It was decided to examine separately the east-west component (u-component) and the north-south component (v-component) of wind velocity. Since the mean square of each component is minimized by the regressions, the mean square vector error is also minimized.

Thus, three parameters were used for estimating wind velocity. These are wind speed and the u and v components of velocity. The u and v components can be used to calculate wind direction. Since predictands relating to wind speed and direction are required at three levels (stack height and plume heights according to Briggs and Djurfors-Netterville), there were a total of nine equations for wind parameters.

Predictands related to wind were obtained from 2352 pilot balloon observations made in the vicinity of the Syncrude oil sands extraction plant during the years 1975 to 1978 inclusive. The annual distribution of these observations is shown in Figure 2. There were relatively few observations in December and from mid-April to mid-June. All data were collected during daylight hours. Most of the observations were made from 0400 to 1700.

3.2 VERTICAL POTENTIAL TEMPERATURE GRADIENT AT STACK TOP

Vertical temperature gradients are required to determine atmospheric stability for plume rise considerations and to calculate the Brunt-Vaisalla frequency in stable conditions. They may also be used to estimate mixing heights.

Temperature gradients for use in developing a forecast scheme were obtained as the average temperature difference over the hundred meters extending from stack top to 283 m. The necessary information was available from 2289 minisonde observations which were generally made at the same time as the pibal measurements. Occasionally minisonde data were missing but temperatures were available from the 90 and 152 m levels of the Tall Tower. Under these circumstances, the Tall Tower data were used to estimate temperature gradients.

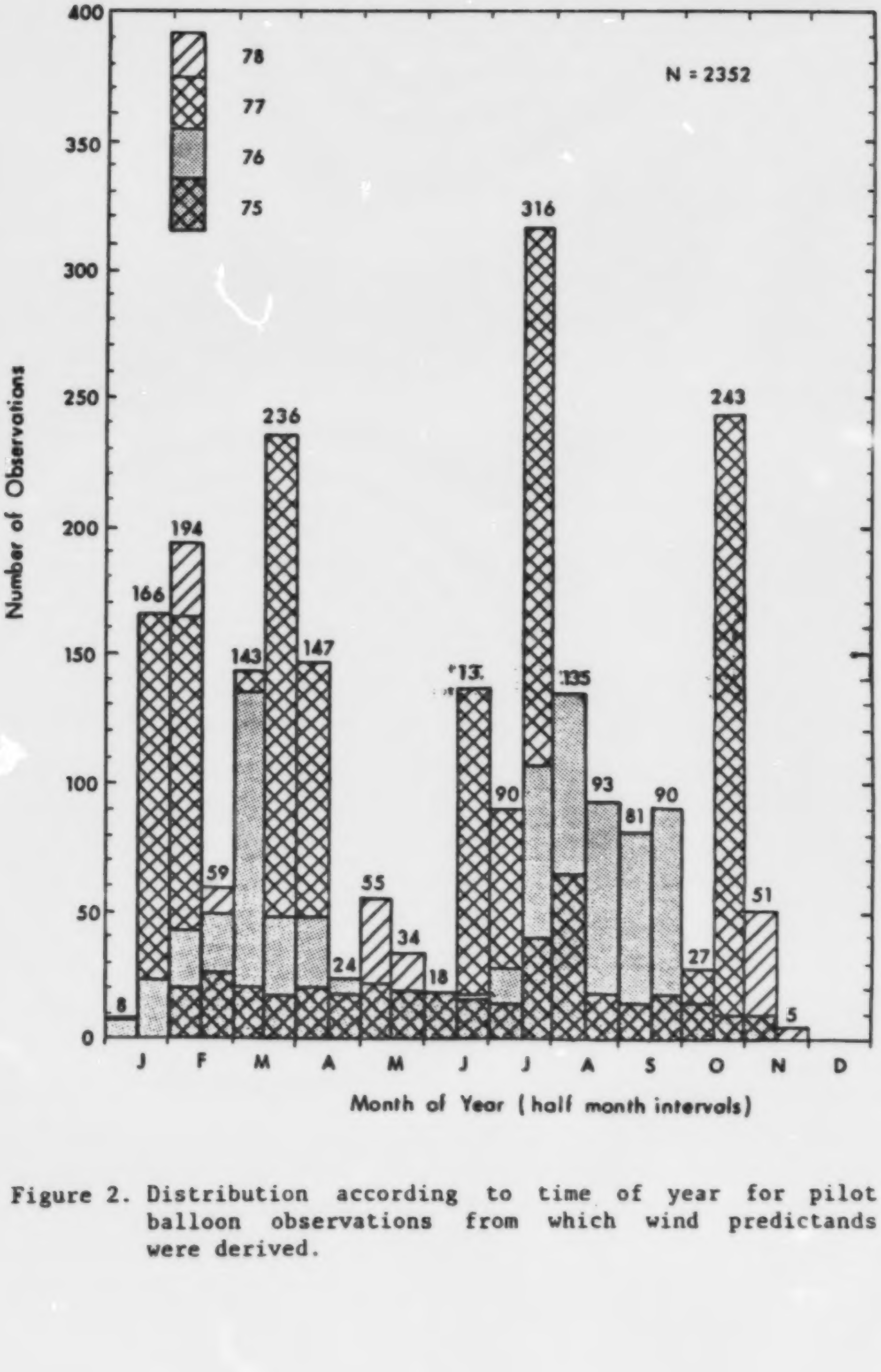

Figure 2. Distribution according to time of year for pilot balloon observations from which wind predictands were derived.

3.3 HEIGHT OF MIXING LAYER

The height and variability of the mixing layer is important in the assessment of fumigation and plume trapping situations. There are two different methods for estimating the mixing height: the conventional method and the kink method.

In the conventional method, the mixing height is the height above ground at which the dry adiabat through the surface temperature intersects the temperature profile. In the kink method, the mixing height is the first point at which the rate of change of potential temperature with height is maximum (Kumar 1979).

Data for mixing depths evaluated by both the conventional and the kink methods were obtained from the 2289 minisonde observations made near the Syncrude oil sands extraction plant.

The forecast scheme will provide estimated values of mixing depths eight hours in advance of real time. Predictor variables will be derived from radiosonde data. The first radiosonde information for the day is obtained at 0500 MST (1200 GMT) and is generally not available until 0600. Therefore, the earliest time for which an eight-hour forecast can be made is 1400. In consequence, mixing depths were evaluated from the minisonde observations only for the hours 1400, 1500, and 1600. During non-winter seasons when the conventional mixing depth may exceed 800 m, its value was taken as the average seasonal maximum value given by Portelli (1977). These values are 1240, 1730, and 870 m for spring, summer, and autumn, respectively.

Of the 2289 minisonde observations, 471 were analyzed for mixing depths. Most of the analyzed observations were made during the winter and early spring.

4. PREDICTORS FOR WIND AND TEMPERATURE

There are a wide variety of possible predictors which might be employed in a forecast scheme. These include both observed and forecast local and regional data as well as time of day and day of year. Locations from which data may be obtained have been shown in Figure 1.

4.1 LOCAL METEOROLOGICAL DATA

Meteorological information related to wind, temperature, and precipitation is collected on an hourly basis at a number of locations in the Fort McMurray area. These include the Fort McMurray airport, the Tall Tower, and a network of monitoring stations (MAPS) operated by Alberta Environment. Only four of these stations have been in operation since April 1980. Data related to cloud cover are available from the Fort McMurray airport. Upper air winds at the Fort McMurray airport are observed by pibals released up to three times per day.

4.2 REGIONAL WIND AND TEMPERATURE DATA

Wind and temperature data at 850 mb (about 1200 m above surface in the Syncrude plant area) can be obtained twice daily for the oil sands area from pressure-height charts, which are based on information provided by the AES radiosonde network. Forecast winds at 850 mb can be obtained from forecast pressure-height charts which are prepared by the AES. Vertical profiles of temperature are available twice daily, at 0000 and 1200 GMT, from AES radiosonde stations at Fort Smith and Stony Plain. These stations lie about 350 km north and 400 km southwest of Fort McMurray, respectively. Their locations are shown in Figure 1.

These profiles were used to estimate hourly mixing depths by modifying the lower portion of the morning sounding (0500 MST) according to two parameters: hourly surface temperatures at a nearby surface station, and temperature change at 700 mb between consecutive soundings. The estimation procedure is described in a paper by Benkley-Schulman (1979).

4.3 TIME PARAMETERS

A suggestion of Glahn and Lowry (1972), regarding time of day and day of year was incorporated in the forecast scheme to reflect diurnal annual cycles. The time of day parameters, T_{day}, were calculated to the relation:

$$T_{day} = \sin \left[(HR-2) \ \frac{\pi}{24} \right] \tag{3}$$

where HR is hour of the day, from 0 to 23.

The time of year parameter, T_{year}, was calculated according to the relations:

$$T_{year} = \sin \left[(DAY-13.5) \frac{\pi}{365} \right] \text{ (non-leap years)} \quad (4)$$

$$T_{year} = \sin \left[(DAY-14.0) \frac{\pi}{366} \right] \text{ (leap year)} \quad (5)$$

where DAY represents the cumulative day of the year (from 1 to 365 or 366).

5. FORECAST EQUATIONS

Observations for predictands were divided in a pseudo-random fashion into two nearly equal size groups. Group A, which contained 1303 observations, was used to develop the forecast scheme. Group B, which contained 1168 observations, was used as verification data for evaluating the forecast scheme. Regression equations were limited to a maximum of 10 predictors. Predictors were selected such that they met three criteria.

- Inclusion of the predictor must result in a reduction of residual variance by at least 0.5%.
- The significance of the predictor included in the equation must be at least 15% as determined by the F statistic.
- After the addition of the predictor to the equation the significance level of each predictor already in the equation must remain at 15% or less.

5.1 FORECAST SCHEME FOR WIND PREDICTANDS

An example of a derived forecast equation is given in Table 1. This table presents the equation for wind speed at stack height. The best predictor was the Fort McMurray surface wind speed at the hour at which the 8-hour forecast will be valid.

Table 1. Equation for estimating windspeed at stack height.

	PREDICTOR				
Parameter	Location	Level	Time	COEFFICIENT	CUMULATIVE INCREASE OF R^2
Constant	+[a]	+	+	1.1588	+
Windspeed	Fort McMurray	surface	8-hour[b]	0.5004	.273
Windspeed	+	850 mb	8-hour	0.2266	.369
Temperature	Fort McMurray	surface	0-hour[c]	0.1036	.420
v-component of velocity	Fort McMurray	plume B[d]	0-hour	-0.0364	.449
Temperature	Fort McMurray	surface	8-hour	-0.0716	.461
v-component of velocity	Mildred Lake	surface	0-hour	-0.3346	.476
Time of day	+	+	0-hour	1.1583	.484
v-component of velocity	Fort McMurray	surface	8-hour	-0.1350	.490
u-component of velocity	+	850 mb	8-hour	-0.0908	.493
u-component of velocity	Fort McMurray	surface	8-hour	0.0976	.496

[a] entry not appropriate for this parameter
[b] 8-hour is the hour at which a forecast will be valid
[c] 0-hour is the hour at which a forecast is made
[d] plume height according to Briggs

Forecast equations were tested using the verification set of data referred to as Group B. Squares of the multiple correlation coefficient calculated using the recommended forecast scheme are shown in Table 2. Correlation coefficients obtained using the derivation data are shown for comparison.

Values of R^2 in Table 6 calculated using the derivation data range from 0.50 to 0.59. The means that 50 to 59% of the total variation of wind speeds and direction components about their mean values are explained by the regression. Values of R^2 are slightly less for wind speeds than for wind direction components. Values of R^2 shown in Table 6 for tests on the verification data range from 0.33 to 0.55. For wind direction components, these values are generally consistent with those calculated using derivation data. However, for wind speeds, R^2 values were slightly lower. Overall similarities in R^2 obtained using both derivation and verification data indicate some degree of stability in the entire data set.

Comparison between predicted and observed wind speeds and directions using the verification data are given in Table 3. The RMS error in wind speeds was about 40% of the mean values. Wind direction RMS errors were about 53°.

5.2 FORECAST SCHEME FOR TEMPERATURE PREDICTANDS

An example of a derived forecast equation for temperature predictands is shown in Table 4. This table presents the equation for predicting mixing depths. Time of year was the most significant predictor.

Forecast equations for temperature predictands were tested using the verification data. Table 5 shows that values of R^2 for temperature gradient data calculated from derivation and verification data are comparable. Success in forecasting mixing heights from the verification data was poor. This is especially true for the kink mixing height for which the negative value R^2 indicates no correlation between predicted and observed values.

Table 2. Squares of the multiple correlation coefficient (R^2) for wind predictands using both derivation and verification data.

LEVEL	WIND PREDICTAND	R^2 Derivation Data	R^2 Verification Data
Stack height	Windspeed	0.50	0.47
	u-component of velocity	0.55	0.54
	v-component of velocity	0.53	0.50
Plume height B[a]	Windspeed	0.54	0.33
	u-component of velocity	0.58	0.49
	v-component of velocity	0.56	0.50
Plume height D[b]	Windspeed	0.52	0.43
	u-component of velocity	0.59	0.50
	v-component of velocity	0.54	0.55

[a] plume height according to Briggs

[b] plume height according to Djurfors-Netterville

Table 3. Comparison between predicted and observed wind speeds and direction.

ELEVATION	PREDICTAND	NO. OF PREDICTIONS	MEAN VALUE		STANDARD DEVIATION		RMS ERROR
			Observed	Predicted	Observed	Predicted	
Stack Height	Speed (ms^{-1})	530	5.2	5.3	2.8	2.0	2.0
	u (ms^{-1})	736	-1.5	-1.4	4.3	2.9	2.9
	v (ms^{-1})	529	-1.4	-1.6	3.5	2.7	2.5
	Direction (°)	529	194	208	85	73	56
Briggs Plume Height	Speed (ms^{-1})	1012	7.7	7.6	4.0	2.9	3.3
	u (ms^{-1})	736	-3.5	-3.5	6.0	4.6	4.3
	v (ms^{-1})	530	-1.5	-1.4	5.2	3.9	3.7
	Direction (°)	530	218	234	81	69	52
Djurfors-Netterville Plume Height	Speed (ms^{-1})	734	7.5	7.4	3.8	2.4	2.9
	u (ms^{-1})	529	-3.4	-3.6	6.1	4.5	4.3
	v (ms^{-1})	529	-1.5	-1.3	5.0	3.6	3.3
	Direction (°)	529	216	232	81	71	51

Table 4. Equation for estimating mixing depth by the conventional method.

Parameter	PREDICTOR Location	Level	Time	COEFFICIENT	CUMULATIVE INCREASE OF R^2
Constant	+[a]	+	+	-39.2983	+
Time of year	+	+	+	737.1585	0.220
u-component of velocity	Fort McMurray	surface	8-hour[b]	43.7379	0.252
Mixing depth	Stony Plain	+	8-hour[c]	0.1409	0.276
Cloud amount	Fort McMurray	surface	0-hour	17.6309	0.287
Temperature gradient	Fort Smith	stack top[d]	8-hour	-12638.5228	0.298

[a] entry not appropriate for this parameter
[b] 8-hour is the hour at which a forecast will be valid
[c] 0-hour is the hour at which a forecast will be made
[d] stack top level is between 183 and 283 m

Table 5. Squares of multiple correlation coefficient (R^2) for temperature predictands using both dependent and independent data.

TEMPERATURE PREDICTAND	R^2	
	Derivation Data	Verification Data
Temperature Gradient at stack height[a]	0.29	0.27
Conventional Mixing Depth	0.30	0.20
Kink Mixing Depth	0.29	-0.16

Comparison between predicted and observed values for temperature related predictands as obtained from the verification data set are given in Table 6. The RMS error for temperature gradients was 1.2°C/100 m. Mixing heights were forecasted with RMS errors which were about 68% of their mean values.

6. DISCUSSION

Regression analyses for wind-related parameters were based on predictands obtained from pibal observations. There are some uncertainties inherent in their measurement as discussed by Netterville-Djurfors (1979). In addition, pibal winds are instantaneous winds which may contain scatter about a mean value. These winds were used in the regression analyses with predictors which for the most part represent winds averaged over a larger time interval. It seems reasonable that the use of site specific, time-averaged winds (from an acoustic sounder) as predictands in the regression analyses could result in higher R^2 values.

Correlation coefficients for temperature parameters are lower than those obtained for wind parameters. Use of predictors other than those considered in this paper may improve the results. These may be either observed meteorological parameters from the region, or predicted parameters from boundary layer models.

Table 6. Comparison between predicted and observed temperature predictands.

PREDICTAND	NUMBER OF PREDICTIONS	MEAN VALUE		STANDARD DEVIATION		RMS ERROR
		Observed	Predicted	Observed	Predicted	
Temperature Gradient at Stack Height (°C/100 m)	1080	0.4	0.4	1.5	0.8	1.2
Conventional Mixing Height (m)	132	802	805	568	311	505
Kink Mixing Height (m)	122	374	302	252	138	270

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STACK DESIGN FOR STABLE AIR FLOW IN COMPLEX TERRAIN

R.D. ROWE[1]

ABSTRACT

This paper is concerned with the problem of plume dispersion in the vicinity of an isolated terrain feature, such as a single hill or ridge. The results of recent experiments designed to determine pollutant dispersion near terrain obstacles in stable atmospheres are reviewed. Two worst case analyses for dispersion in the air layer that crosses over a terrain obstacle in very stable low Froude number flow are developed. It is suggested that one possible critical design condition for a stack would be to find the effective stack height such that the plume just reaches this layer in the most stable winter atmosphere that is likely to occur. Alternatively, if it is required that the plume should always be placed well into this flow layer, then it is shown that the plume rise at 1 m/s in the most stable atmosphere should normally be at least 1½ times the height of the terrain crest above the stack top. These ideas are expressed in graphical form, using a new graph which is presented for the first time at this symposium.

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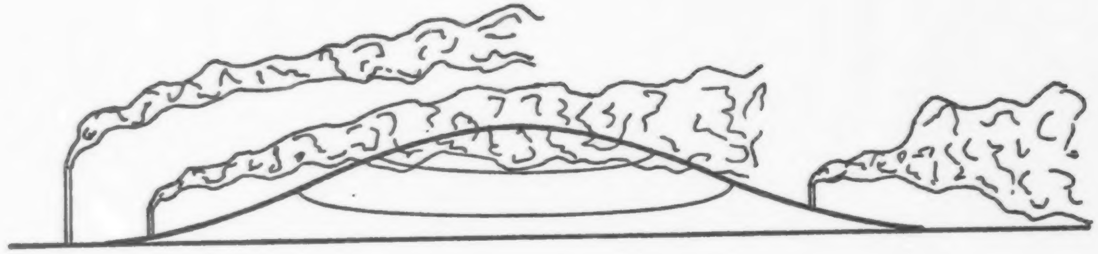
1. INTRODUCTION

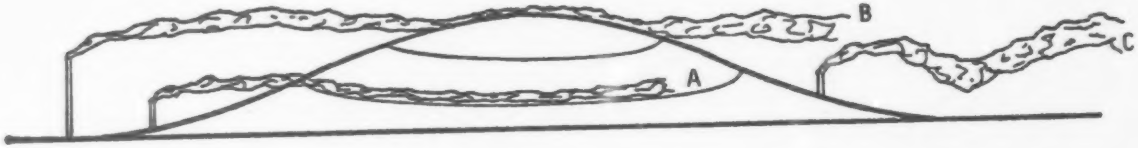
Atmospheric dispersion in an area of complex topography is normally much more complicated than that over flat ground. Various aspects of this problem are currently being investigated by several research groups, e.g. the EPA's Small Hill Impaction Study (Lavery et al. 1982). The determination of stack height for a site in level or mildly undulating terrain is now reasonably well understood and the neutral stability atmosphere is normally used for worst case analysis (Pasquill 1974). However, the highly stably stratified atmosphere often produces the poorest dispersion conditions for a site in rugged terrain, and horizontal trajectory models with effectively direct impaction on the terrain are used by some regulatory agencies, e.g. the EPA Valley model (Burt and Slater 1977).

This paper is concerned with the problem of plume dispersion in the vicinity of an isolated terrain feature, such as a single hill or ridge. A sketch of possible plume dispersion patterns over a three-dimensional hill in neutral and stable stratification is provided in Figure 1; this figure has been taken from an EPA report by Hunt, Snyder, and Lawson (1978). For neutral atmospheres all of the air flows over the terrain feature, but the diffusion is significantly greater than that for highly stratified atmospheres. For highly stratified atmospheres, the lower layers are constrained to flow around the terrain in essentially horizontal planes, as shown by plume A, and only the upper layers can flow over the feature (plume B). Downstream of the terrain, the plume dilution rate is increased in the wake for neutral stratification, or the plume may oscillate vertically in the lee waves for stable stratification (plume C).

The upwind-side flow patterns have been confirmed by three different field experiments, using smoke timelines, tetroon flights, and plume photography, which we have undertaken at the Copithorne ridge site (Rowe et al, 1982). This ridge is reasonably two-dimensional with a length-to-width ratio of about 5. In particular, our data show that for highly stratified atmospheres the lower air layer does indeed flow around this fairly long obstacle.



(A) NEUTRAL STRATIFICATION



(B) STABLE STRATIFICATION

Figure 1. Sketch of plume behaviour over a three-dimensional hill in neutral and stable stratification. This diagram has been taken from Hunt, Snyder, and Lawson (1978).

The lee-side streamline patterns can be very complicated as has been shown by the laboratory water and wind tunnel studies of Hunt and Snyder (1980) (see Fig. 1 on p. 672 of their paper). Some indication of the downwind structure has been provided by our tetroon flights (Rowe, Benjamin, and Chung 1981), but we were not able to resolve the downwind flow field with anything like the detail given by Hunt and Snyder (1980).

2. INTERFACE ELEVATION

A schematic diagram of the two layers in highly stable flow is given in Figure 2. A typical streamline in the upper layer with an upstream elevation H_s, and the dividing streamline between the two layers at an elevation H_d are shown. Assuming that the flow is inviscid and that the pressure set up by fluid acceleration can be ignored, it can easily be shown (see, for example, Rowe 1980) that the vertical distance down from the crest of the terrain to the interface between the two layers is given by:

$$h - H_d = \frac{U}{N} \qquad (1)$$

where h = elevation of terrain crest;

H_d = elevation of dividing streamline between the two layers (above the base of the terrain feature);

U = wind speed (at elevation H_d);

$N = \left(\frac{g}{T_d} \frac{d\theta}{dz}\right)^{\frac{1}{2}}$ = Brunt-Vaisala frequency, which is the natural frequency of oscillation of an air parcel;

T_d = absolute temperature at elevation H_d;

$\frac{d\theta}{dz}$ = vertical potential temperature gradient.

The Froude number for stable flow with a characteristic length scale h is given by:

$$F = \frac{U}{Nh}$$

and Equation (1) can therefore be written in an alternative form:

$$H_d = h(1 - F) \qquad F \leq 1 \qquad (2)$$

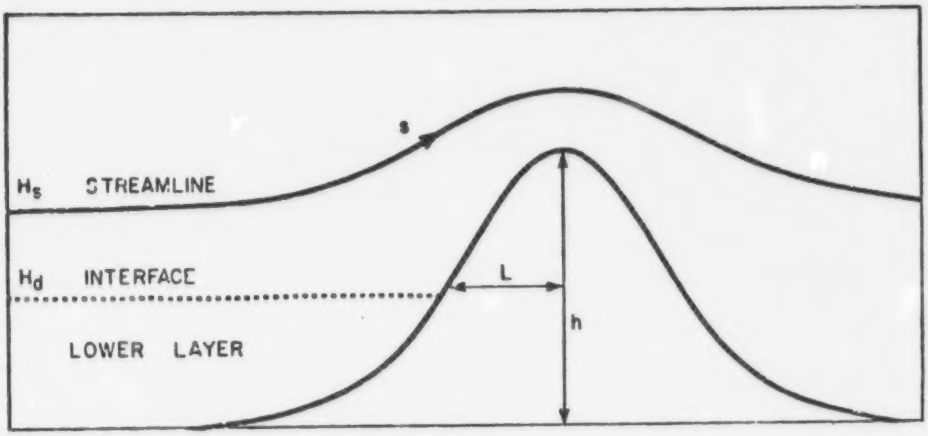

s
H_s STREAMLINE
H_d INTERFACE
L
h
LOWER LAYER

Figure 2. A schematic diagram of a stable flow streamline in the upper layer across a terrain obstacle.

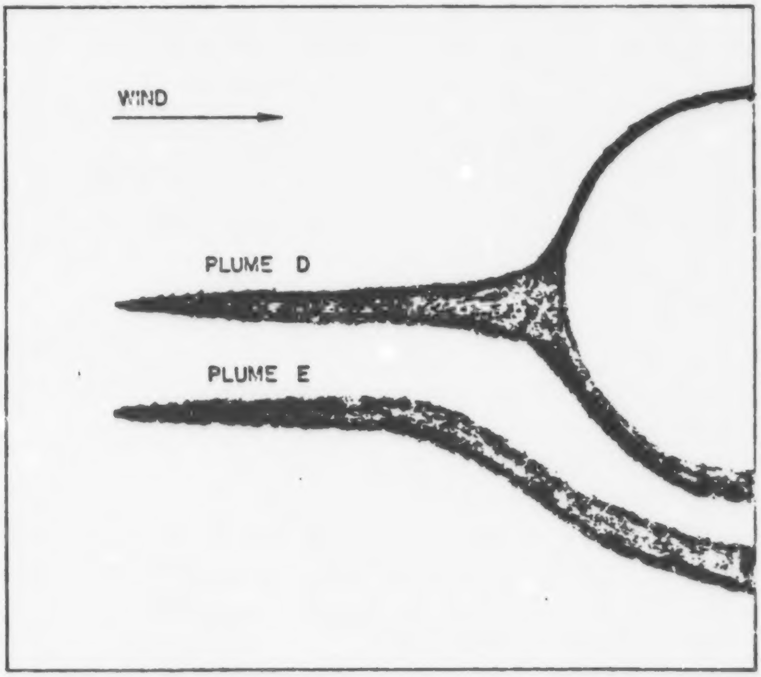

WIND
PLUME D
PLUME E

Figure 3. A sketch of plume dispersion in the lower layer around a circular hill. Plume D is close to the stagnation streamline.

When the Froude Number F is greater than one ($F > 1$) all of the air flows over the terrain obstacle.

3. LOWER LAYER FLOW

If the effective stack height is lower than the interface elevation, then the plume follows the lower layer flow. In support of horizontal trajectory models, such as the EPA Valley model, it should be noted that it is certainly possible for the plume in the lower layer to impact on the terrain feature if the stagnation streamline passes close to the location of the stack, as is shown in Figure 3. In this case, the plume is imbedded in flow around one or both sides of the obstacle (plume D). The flow field on the upwind side at a given elevation can be described to a very good approximation by two-dimensional potential flow in the horizontal plane. This theoretical approach has been used by Hunt, Puttock, and Snyder (1979); they showed that the maximum ground level concentration is given approximately by the centreline plume concentration immediately upwind of the obstacle, rather than twice this value as prescribed in the EPA Valley model. An image source is incorrectly used in the EPA Valley model because the plume is not primarily diffused to the ground but rather it is advected onto the terrain.

Most of the time when the wind direction takes the plume towards the terrain feature the plume flows with the streamlines around one side, and it does not normally contact the feature because of the slow rate spread of the plume by turbulent diffusion in a stable atmosphere (plume E in Figure 3). A model to describe this type of behaviour is currently being developed at Environmental Research and Technology, Inc. (Venkatram et al. 1982). However, since it is certainly possible for the narrow highly stable plume to impact on the terrain occasionally, if it is at all possible the effective stack height should be made large enough for the plume to reach the upper layer flow at all times.

The most stable atmospheres occur during the winter with snow cover and clear skies. Since vegetation is normally dormant in the winter, it is suggested that a critical design condition for a stack might be to make the effective stack height just large enough for the plume to reach the upper layer flow in the most stable atmosphere that is likely to occur, i.e., for the situation shown by plume B in Figure 1. For this design condition, the plume would then be lifted clear of the terrain in the less stable atmospheres during the rest of the year when vegetation is active. For southern Alberta, it is unlikely that the Brunt-Vaisala frequency N would exceed 0.01 cps, i.e., a maximum vertical temperature gradient of about 10°C/100 m (see for example, Leahey 1977). Once the highest value of N is fixed, the critical wind speed can then be found for a given terrain and stack combination; the derivation of this relation is provided in Section 6.

4. UPPER LAYER FLOW

We have proposed that the flow in the upper layer that passes over the terrain should be modelled by potential flow (Rowe 1980). Hunt and Snyder (1980) have provided numerous data from laboratory experiments for the streamline elevation above the top of a three-dimensional bell-shaped hill as a function of Froude number. Rowe, Lee, and Havlena (1980) have replotted these data using the appropriate coordinates for the layer that flows over the hill; only those data points with $F < 1$ had to be moved to take account of the new axes. It was found that there is still considerable scatter of the data points for $F < 1$, and thus the flow structure in the upper layer is evidently dependent on the Froude number. However, the curve through the $F = 1.0$ data does provide a reasonable average estimate for most of the $F \leq 1$ points.
The elevation of the $F = 1.0$ data above the hill top have only about one half of the values predicted by potential flow theory; but, as shown by the $F = 1.6$ data points, the Froude number does not have to be much greater than one for the streamlines to approximate potential flow.

Although the laboratory data of Hunt and Snyder show that potential flow overestimates the elevation of streamlines above a

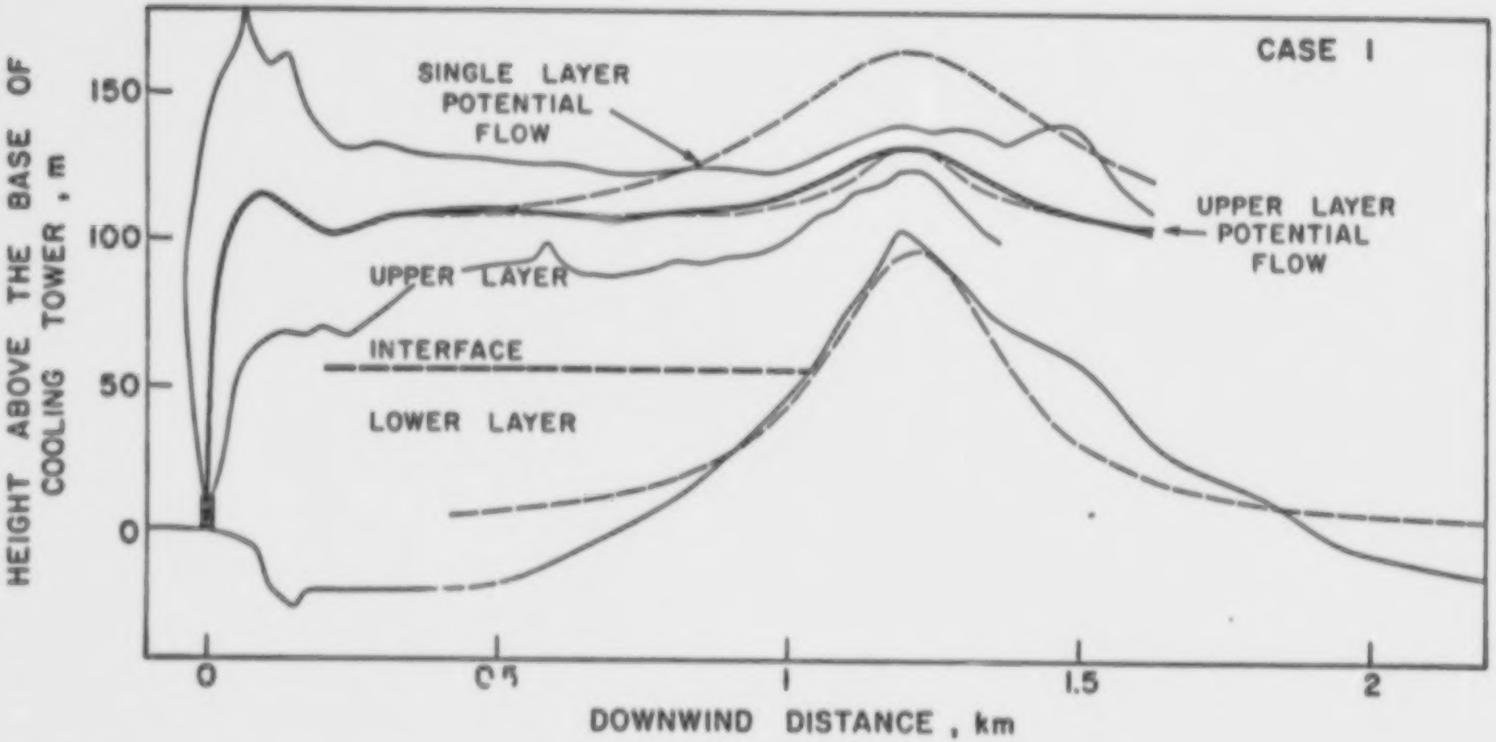


Figure 4 Cooling tower plume outline and centreline trajectory. The potential flow streamlines for both the single-layer and the two-layer models are also shown. The dashed curve next to the ridge denotes the theoretical bell-shaped ridge used in the potential flow calculations. (Rowe et al, 1982).

hill top when $F \leq 2$, potential flow is able to account for gross terrain differences in a very simple manner, and can handle three-dimensional as well as two-dimensional flow situations. Therefore, it is recommended that the streamline elevations on the windward side and the top of terrain features in the layer that crosses the obstacle (whether it be the upper of two layers or a single layer) should be calculated using potential flow theory. The flow structure on the lee side of terrain obstacles is much more complicated and potential flow should not be applied on the downwind side.

An example of the application of potential flow to the upper layer flow across the Copithorne ridge is shown in Figure 4. The flow is made visible in this case by photography of the ice crystal plume from the cooling tower at the Shell Jumping Pound gas plant (Rowe et al. 1982). It should be noted that the environmental lapse rate was not measured and that the elevation of the interface between the two layers H_d was determined by making the potential flow streamline in the upper layer fit the experimental plume centreline at the crest of the ridge as well as at the effective plume height upwind of the ridge.

If it is required that the plume should always be placed well into the upper layer flow, then it is shown in Section 6 that the plume rise at 1 m/s in the most stable atmosphere should normally be at least 1½ times the height of the terrain crest above the stack top. It is also shown in Section 6 that the cooling tower plume shown in Figure 4 satisfies this rule very closely. In this case, the plume would then probably clear the crest of the terrain feature completely, because the diffusion of the plume about its centreline is small for this type of atmosphere. However, the plume could still be brought down close to the ground in the lee-side flow (Rowe, Benjamin, and Chung 1981). Increased turbulence, flow separation, or wave breaking would also be required to bring the pollutant plume in contact with the ground in this situation. Significant lee-side concentrations of an SF_6 tracer have recently been observed by Lavery et al (1982) for highly stable flow over a circular shaped hill called Cinder Cone Butte. Further cooling tower plume photography experiments are currently in progress at the Copithorne ridge to see whether this type of behaviour can be demonstrated at this site.

5. NEUTRAL FLOW

If the plume height is significantly greater than the elevation of the terrain feature, then the plume will probably clear the lee waves behind the topography. In this situation, the more unstable neutral atmosphere which enables the pollutant to be diffused to the topography would probably be the worst case (Figure 1). In 1973, a new 102 m high incinerator stack at the Shell Jumping Pound gas plant was designed for this atmospheric condition using the potential flow approach (Leahey and Rowe 1974).

6. PLUME ELEVATION GRAPH

The final plume rise h_r in a moving stable atmosphere given by (Briggs, 1969):

$$h_r = A\left(\frac{Q_H}{UN^2}\right)^{1/3} \qquad (3)$$

Where A = a constant;

Q_H = heat emission rate.

It should be noted that Equation (3) applies only to a moving atmosphere and is therefore not valid for wind speeds much less than 1 m/s.*

For fixed Q_H and N:

$$\frac{h_r}{h_{r1}} = \frac{1}{U^{1/3}} \qquad (4)$$

where h_{r1} is the plume rise at a wind speed of 1 m/s for the fixed values of Q_H and N considered. Dimensionless plume rise h/h_{r1} is plotted as a function of wind speed in Figure 5.

The elevation of the interface between the two layers above the physical stack height is given by Equation (1) in Section 2, that is:

* please see last page

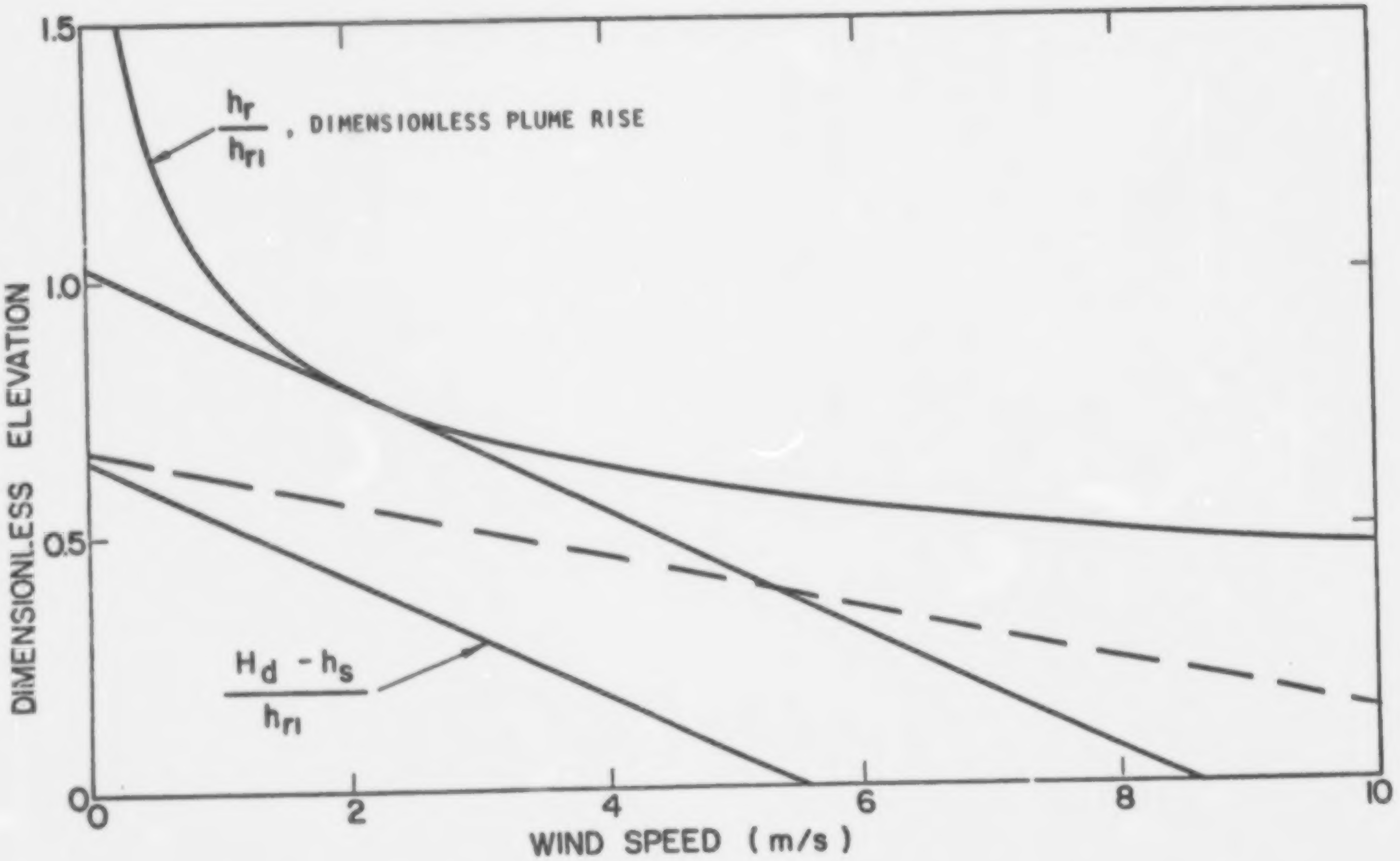


Figure 5. Dimensionless elevation (plume rise or interface elevation above stack top) as a function of wind speed. The Brunt-Vaisala frequency has a fixed value. h_{r1} is the plume rise in the stable atmosphere at 1 m/s.

$$H_d - h_s = (h - h_s) - \frac{U}{N} \qquad (5)$$

where h_s = physical stack height.

If these distances are made dimensionless by dividing by h_{r1}, the above equation becomes:

$$\frac{H_d - h_s}{h_{r1}} = \frac{h - h_s}{h_{r1}} - \frac{U}{Nh_{r1}} \qquad (6)$$

$(H_d - h_s)/h_{r1}$ as a function of U can therefore be plotted as a straight line, which intersects the vertical and horizontal axes at $(h - h_s)/h_{r1}$ and $N(h - h_s)$ respectively on Figure 5.

The dimensionless elevation of the plume above the interface between the two layers $(H_s - H_d)/h_{r1}$ (where $H_s = h_r + h_s$) is then given by the vertical distance between the dimensionless plume rise curve (Equation 4) and the dimensionless interface elevation above the stack top straight line (Equation 6).

For example, consider the application of Figure 5 to the cooling tower plume shown in Figure 4. For this case:

U = wind speed = 2.7 m/s;
U/N = 42 m (where N = Brunt-Vaisala frequency);
h_s = physical stack height = 11 m;
h_r = plume rise = 95 m;
h = ridge crest elevation = 97 m.

The Brunt-Vaisala frequency N = 2.7/42 = 0.064 rad/s = 0.010 cps, i.e.,about the most stable atmospheric condition that is likely to occur in southern Alberta (Section 3). The plume rise at 1 m/s, $h_{r1} = 95 \times (2.7)^{1/3} = 132$ m. The straight line for this case is shown on Figure 5; this line intersects the vertical axis at $(h - h_s)/h_{r1} = (97 - 11)/132 = 0.65$ and the horizontal axis at N $(h - h_s) = 0.064\ (97 - 11) = 5.5$ m/s.

It can be seen on Figure 5 that this cooling tower plume would be placed well into the upper layer for any wind speed. It can also be seen that when the plume rise at 1 m/s is about 1½ times the height of the terrain crest above the stack top (i.e.,when $(h - h_s)/h_{r1} = 2/3 = 0.67$), the plume would be placed well into the upper layer flow for quite large values of the intersection with horizontal axis at $N(h - h_s)$. This rule for $h - h_s = 200$ m (i.e., $h_{r1} = 300$ m) and $N = 0.010$ cps is shown by the dashed straight line on Figure 5.

As a final example, the theoretical crest height of a terrain obstacle such that this cooling tower plume just reaches the upper layer is calculated. For given h_{r1} and N, the slope of Equation (6), which is equal to $-1/(Nh_{r1})$, is fixed. Therefore, this problem is solved by drawing a parallel straight line which is tangent to the dimensionless plume rise curve on Figure 5. This straight line intersects the vertical and horizontal axes at 1.02 and 8.6 m/s respectively, so the maximum crest elevation above the top of the stack, $h - h_s = 1.02\ h_{r1} = 8.6/N = 135$ m. This critical situation occurs at a (critical) wind speed of about 2.2 m/s for this example.

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8. ACKNOWLEDGEMENTS

The plume photography and tetroon flights experiments at the Copithorne ridge (Rowe et al. 1982) were supported by a cooperative grant from the Alberta Environmental Research Trust and Shell Canada Resources Limited. Further experiments to investigate the dispersion of the cooling tower plume on the lee side of the Copithorne ridge are currently supported by a new grant from the Alberta Environmental Research Trust.

* It should also be noted that Equation (3) should only be used for single-phase plumes, and is therefore only an approximation for the cooling tower plume.

NO_x CONTROL TECHNOLOGY FOR COMPRESSOR ENGINES

MICHAEL J. ZELENSKY, P. Eng.[1]

ABSTRACT

(Only Executive Summary was submitted)

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[1] Western Research, Division of Bow Valley Resource Services Ltd.

1. EXECUTIVE SUMMARY

1.1 INTRODUCTION

Compressor engines are used extensively in the production and transmission of oil and gas. These engines are natural gas fueled and are typically large-bore, spark-ignited reciprocating engines or gas turbines. When compared to other combustion devices, compressor engines are major emitters of oxides of nitrogen (NO_x). Alberta Environment has estimated that approximately 35% of all NO_x emitted in the province result from the operation of compressor engines. This is due to the large number of units scattered throughout the province and the significantly higher NO_x emissions per unit of fuel input. The conditions which promote NO_x formation, high temperatures, available oxygen and sufficient time, all exist in compressor engines.

This study assesses the state-of-the-art of NO_x control technology for compressor engines and summarizes the control options which are technically proven and economically feasible. A strategy for a practical means of reducing NO_x emissions from compression facilities within the petroleum industry can then be developed with the results.

NO_x emissions can be reduced from current uncontrolled levels using demonstrated technology. Two approaches can be taken, NO_x formation can be prevented by combustion modifications or NO_x can be removed from the exhaust, after it has been formed, by exhaust gas treatment. If used together the reductions are additive. Combustion modifications minimize any or all of the variables (temperature, available oxygen, time) which control the NO_x formation rate and can be made through operational adjustments and/or hardware additions. Catalytic exhaust gas treatment systems remove NO_x from the exhaust by reducing it to N_2.

Table 1 summarizes the effectiveness of NO_x control techniques which are technically proven and economically feasible. Decreases in NO_x emissions are usually accompanied by increases in unburned hydrocarbon and carbon monoxide emissions and increased fuel consumption.

Table 1. Summary of recommended (NO_x) control techniques for compressor engines,

NO_x Control Technique	Percent Reduction Achievable
RECIPROCATING ENGINES	
Operational Adjustments	
Combinations of: o Air-to-fuel ratio change o Retard ignition o Reduced inlet manifold temperature o Derate power output	up to 40
Hardward Additions	
o Exhaust gas recirculation	40-60
o Combustion chamber and ignition design modifications	60-90
Exhaust Gas Treatment	
o Selective catalytic reduction lean burn engines only	80+
o Nonselective catalytic reduction rich burn engines only	90+
GAS TURBINES	
Hardware Additions	
o Dry controls	40-60

1.2 RECIPROCATING ENGINES

Operational adjustments can be made by the operator to existing engines. However, the advice of the manufacturer should be obtained since the effectiveness varies considerably with engine design. Reduction of 40% are considered to be the limit before resulting changes to engine performance, fuel consumption and CO emissions become unacceptable. Combinations of air-to-fuel ratio changes, retarding the ignition and reducing the inlet manifold temperature are used by manufacturers to minimize the fuel penalty while maximizing the NO_x reduction from new engines. Derating an engine, by limiting the power output to a level lower than that for which it was designed, is not applicable to existing installations unless the engine was over-rated when installed or compression requirements have decreased.

Hardware additions are now becoming available from engine manufacturers as options on new engines or for retrofit to existing engines during rebuilding. Combustion chamber and ignition design modifications may be able to reduce emissions substantially without increases in fuel consumption.

Catalytic exhaust gas treatment systems replace the muffler and can be installed on new or existing facilities. The catalyst system used depends on whether the engine is running rich (less than 1% O_2 in exhaust)or lean (greater than 1% O_2 in exhaust). Generally, all four stroke naturally aspirated and a few four stroke turbocharged engines can be operated as rich burn engines. All two stroke engines and a few four stroke turbocharged engines must be operated as lean burn engines. Nonselective catalytic reduction systems, although more effective than selective catalytic reduction systems, cannot be applied in a cost effective manner to lean burn engines.

Nonselective catalytic reduction utilizes CO, H_2, and CH_4, which naturally occur in the exhaust, as the reducing agents. To provide a sufficient supply of reducing agents the air-to-fuel ratio of the engine must be decreased (richened) from the manufacturers setting. Both CO emissions and fuel consumption will increase as a result. Over 100 systems have been installed in the United States and catalyst suppliers guarantee 90% NO reduction across the converter for one year.

Selective catalytic reduction requires the injection of NH_3 into the exhaust stream upstream of the catalyst bed. The NH_3 preferentially reacts with the NO_x in the presence of O_2. An NH_3 storage and control system is required. The engine can be set up for optimum performance. The catalyst and control systems are currently being demonstrated. Guaranteed NO_x reductions of 80% across the converter are expected.

1.3 GAS TURBINES

Hardware additions in the form of improved combustor design are the only technically proven and economically feasible method of reducing NO_x emissions from gas turbine compressor engines. The technique, known as dry control (as opposed to wet control or water injection), can achieve NO_x reductions in excess of 40%. Combustor modifications are incorporated in new turbine designs and may be available for retrofit to existing units. Wet controls are not considered feasible because of the problems associated with water supply. Operational adjustments cannot be made because of the inherent design. Selective catalytic exhaust gas treatment systems are not economically feasible due to the large volumes of exhaust gas.

It is also important to note that in their uncontrolled states, current gas turbines emit about an order of magnitude less NO_x per unit of power output than reciprocating engines. However, a typical turbine powered compression facility has about an order of magnitude greater power than a typical reciprocating engine powered facility.

1.4 COSTS

If ground level NO_x concentrations resulting from the operation of compression facility exceed government objectives, either the stack height can be increased or the NO_x emission rate can be decreased. At-source NO_x control techniques are environmentally more favourable and may be economically justifiable when compared to higher exhaust stacks.

Capital costs of compressor engines will increase by about 5 to 20% due to the additional hardware and/or catalytic exhaust gas treatment system. Operating costs may increase by about 5% due to increased fuel consumption. Detailed cost estimates were not made in this study and would have to be investigated by the user.

The detailed report will be made available by the Alberta Petroleum Industry/Government Environmental Committee. Please contact the author for more information.

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ALBERTA AMBIENT AIR QUALITY STANDARDS FOR SULPHUR DIOXIDE PROTECT THE ENVIRONMENT BUT DESTROY THE CREDIBILITY OF ALBERTA'S SCIENTISTS

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ABSTRACT

Albertans quite rightly assume that there are scientifically sound reasons for the selection of the Alberta Ambient Air Quality Standards for sulphur dioxide. They fear that violations of the Standards endanger the environment, and they become sceptical when government spokesmen repeatedly assure them that, in spite of recorded violations of the Standards, scientists have not observed or measured damage to vegetation and soils in the immediate vicinity of the continuous monitors and no acid rain has fallen in Alberta. Government assurances such as these are incompatible with the perceived significance of Alberta standards violations, and help to destroy the credibility of Alberta's scientists. The public must be informed that a doubling of the sulphur dioxide concentrations allowed in the Alberta Standards represents the Federal Maximum Acceptable Levels for this gas which, by definition, adequately protects the environment. The Federal Maximum Acceptable Levels for sulphur dioxide were determined after a careful study of available world literature by National Research Council scientists between 1970 and 1972.

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1. INTRODUCTION

Albertans quite rightly assume that there are scientifically sound reasons for the selection of air quality standards and that violations of these standards endanger the environment. It should come as no surprise that concerned citizens become sceptical when government spokesmen repeatedly explain that, in spite of recorded violations of Alberta Ambient Air Quality Standards for sulphur dioxide, no acid rain has fallen in Alberta, no acidification of soils has been found to occur, and no vegetation has been injured. In general, scientists involved in pollution research or monitoring work agree that this information is correct: that the environment has not been damaged as a result of recorded violations of the Standards. However, government assurances are incompatible with the perceived significance of Alberta Ambient Air Quality Standards violations. Eventually the public will conclude that scientists involved in environmental matters in Alberta are concealing the facts. After each accusation and denial, the credibility of Alberta's scientists erodes a little.

1.2 AIR QUALITY STANDARDS, CONTINUOUS MONITORS, AND EMISSION STANDARDS

In this presentation I am addressing myself to air quality standards. More specifically, I am addressing myself to atmospheric sulphur dioxide levels as they occur throughout the environment, not as they are measured at a few fixed locations by continuous air quality monitors.

I am not suggesting that continuous air quality monitors operating on a few fixed locations provide a measure of air quality over many hundreds of square miles surrounding the fixed locations of the monitors. I believe that, in forest environments, air quality monitors are of limited use. Their main advantage is their complete objectivity. I believe that the miles and miles of printout or charts issuing from continuous air quality monitors may be misleading. We tend to extrapolate sulphur dioxide concentrations recorded by a few monitors at fixed locations to the hundreds of square miles surrounding them.

I have published my thoughts on the need to monitor the effects of potentially harmful emissions on the receiving environment as long ago as 1972 (Loman et al. 1972). This is now known as "biomonitoring".

To be effective, biomonitoring of the receiving environment is required as long as potentially harmful compounds are emitted from industrial plants. Biomonitoring, therefore, requires a continuing commitment to financial support by the federal and provincial governments, and by the private sector. In my own experience, only the private sector has been consistent in its financial support. On the other hand, we have all experienced the on-again, off-again policy for financial support by the two levels of government.

Neither am I talking about emission standards. I believe that emission standards should remain as they are. Today, after the installation of the most technologically advanced and economically feasible pollution control devices, emission rates are determined that will prevent ground level concentrations from exceeding the Alberta Standards (the Federal Maximum Desirable Levels) under normal operating and weather conditions.

1.3 THE CREDIBILITY OF ENVIRONMENTAL SCIENTISTS IN CANADA AND IN ALBERTA

During a symposium sponsored by the Alberta Society of Professional Biologists, Dr. P.D. McTaggart-Cowan (1980) warned us that "environmental scientists who work for the government have zero credibility with the public because politicians have zero creditility and government scientists are tarred and feathered with the same brush". He further stated that the public "assumes that university scientists are self-serving, that they are not going to bite the hand that feeds then, hence will not upset the Ministers responsible for their already meager funding". Dr. McTaggart-Cowan finally said that the public assumes that "industry hires scientists to protect corporate interests. Whether or not the above is correct is not the question ... this is what is perceived to be going on".

According to McTaggart-Cowan, there are three credible organizations left in Canada. They are the National Research Council, the Science Council of Canada, and the Royal Society of Canada. Here McTaggart-Cowan's concern becomes interesting, because it is unlikely that the "public" either knows or cares that there are three scientific organizations in Canada called the National Research Council, the Science Council of Canada, or the Royal Society of Canada. Only scientists are likely to know about the existence of these organizations. If the public knew that these scientific organizations existed, they would not know whether they consisted of government scientists (with zero credibility) university scientists (who are self-serving), or scientists in the private sector (who are protective of corporate interests but have made major contributions to science). There are, in fact, no other categories of living scientists except the retired who could belong to these credible organizations. Or did McTaggart-Cowan describe the prejudices that one category of scientists has for the other two? His own subjective view is as follows: "when you add up all scientists in Canada with zero credibility, that leaves very few in this country who are still credible in environmental matters, and my reading of the situation suggests that the government in Ottawa seems determined to keep it that way". Divide and Rule! But who are "they in Ottawa" who would understand enough environmental science to even suggest such Machiavellian policy?

I would suggest that Alberta scientists must take their credibility very, very seriously, and must pay considerable attention to providing the public with information that is consistent and not contradictory. This brings us back to the Alberta Ambient Air Quality Standards for sulphur dioxide in Alberta.

2. ALBERTA'S CLEAN AIR ACT

First, the Alberta Ambient Air Quality Standards for sulphur dioxide are established in Alberta's Clean Air Act. It is therefore inevitable that somebody will step forward who wishes to test the provincial government's determination to prosecute violations of existing laws. This is not so strange. After all, in the Canadian public school system, boys and girls are encouraged to ask questions such as, "Why bother having laws if they are not enforced?" But on the other hand, they have also seen the Television series "This is the Law", in which the absurdities of some laws in Canada were exposed. So Canadians know that our laws are not written on stone and can be challenged.

We must recognize then, that Alberta Ambient Air Quality Standards violations for sulphur dioxide are perceived by the public as being damaging to the environment. And we must concede that this is a perfectly reasonable assumption. I am convinced that the time is now, at the beginning of an explosion of industrial development in Alberta, to review the history of the establishment of the Federal Clean Air Act of 1972, and its relation to the Alberta Clean Air Act of 1975; to study the definitions of the Federal Maximum Acceptable and Maximum Desirable Levels for sulphur dioxide in terms of protection against damage to the environment; and to consider changing the Alberta Clean Air Act in line with the Federal Clean Air Act.

3. THE FEDERAL CLEAN AIR ACT

In a nutshell, this is what we must consider: In 1970, the Cabinet of the Government of Canada assigned to the National Research Council (one of the three only organizations with any credibility left, according to McTaggart-Cowan) the task of assessing all known scientific criteria for environmental quality. This task was carried out by six working sub-committees, one of which considered air quality criteria. National Air Quality objectives were proposed by the Department of the Environment in the Canada Gazette of November 13, 1971, and comments were invited from interested individuals and organizations. The proposed objectives were reviewed, and on December 16, 1972, National Ambient Air Quality Standards were published in the Canada Gazette for sulphur dioxide, particulate matter, carbon monoxide, and total oxidants.

Under the Federal Clean Air Act, the National Ambient Air Quality Objectives were designed to protect public health and welfare by setting limits on levels of pollutants in the air. The Clean Air Act calls for three levels of Air Quality Objectives for each major air pollutant. In increasing order of concentration they are: 1) Maximum Desirable Levels, 2) Maximum Acceptable Levels, and 3) Maximum Tolerable Levels. The National Ambient Air Quality objectives were published for the Maximum Desirable and Maximum Acceptable Levels, but not for the Maximum Tolerable Levels for sulphur dioxide, particulate matter, carbon monoxide, and total oxidants, in the Canada Gazette of December 16, 1972.

How are these pollution levels defined? The most rigorous are the Maximum Desirable Levels which define the long-term goals for air quality, and "provide the basis for an anti-degradation policy for the unpolluted parts of the country" and for continuing development of control technology. In other words, in the industrialized parts of Canada, the long-term goal is to achieve these lowest pollution levels, whereas in the unindustrialized parts of Canada, the installation of the most efficient and economically feasible pollution control devices in newly developing industries are intended to maintain ambient air quality at or below these lowest pollution levels. In Alberta, the Alberta Ambient Air Quality Standards for sulphur dioxide are at present identical with the Federal "Maximum Desirable Level", the most rigorous of the National Ambient Air Quality Levels for sulphur dioxide. Does an "exceedence" of the Federal Maximum Desirable Levels damage the environment? The answer is: not necessarily. How high must an "exceedence" of the Federal Maximum Desirable Level or the Alberta Standard be before damage to the environment can be expected? The "exceedence" must be more than the next higher pollution level, the Federal Maximum Level, which is 100% higher than the Federal Maximum Desirable Level or the Alberta standard. Why is this so?

The Federal Maximum Acceptable Level is defined as follows: "The Maximum Acceptable Levels are intended to provide adequate protection against sulphur dioxide effects on soil, water, vegetation, materials, animals, visibility and personal well-being". The Maximum Acceptable Levels were arrived at after a thorough study and interpretation of all available scientific information pertaining to the effects of the environment. It represents the realistic objectives today (as explained in the Canada Gazette of December 16, 1972) for all parts of Canada. When these levels are exceeded, control action by a regulatory agency is indicated."

This is precisely the information that the public requires in order to make sense of what is to it contradictory information. The public needs to know that only if violations exceed 100% more than the Alberta Standards, is there cause for concern. It also needs to know that the sub-committee responsible for researching the world literature on sulphur dioxide effects consisted of National Research Council scientists (just in case a few might question their credibility). The public should also know that the National Research Council's interpretations of the world literature have, in general, been confirmed by scientists in Alberta who have been involved in research and/or monitoring work in the vicinity of sour gas processing plants and the tar sands plants. Quickly, some propaganda for biomonitoring. Government spokesmen have quite rightly relied on the results of biomonitoring reports and research in areas downwind from incinerator stacks, rather than on the perceived (but imaginary) damaging effects of violations of the Alberta Standards.

4. CONCLUDING REMARKS

In my own experience, even senior scientists have confused emission rates with Ambient Air Quality Standards. I am not advocating industries to increase emission rates. What I am saying is this: That when the most technologically advanced and economically practicable control devices have been installed, and emission rates have been determined that will not cause ground level concentration to exceed the Alberta Standards (the Federal Maximum Desirable Levels) under normal operating and weather conditions, the law is changed, so that "exceedences" of these levels, to be called Alberta Maximum Desirable Levels, are not called violations, either "in house" or in the media, until the Federal Maximum Acceptable Levels are exceeded. I also recommend that this terminology, as well as the definition of the Federal Maximum Acceptable Levels in terms of the protection of the environment be explained to the public in future press releases.

The whole purpose of the Clean Air Act is to protect the environment. The purpose of the Act is not to destroy the credibility of Alberta's scientists; nor is it the purpose of the Act to expose industry to harassment with a law that is broken when sulphur dioxide levels exceed 50% of the levels that are still considered to be protective of the environment.

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KEYNOTE ADDRESS

ACID RAIN AND FOREST PRODUCTIVITY

S.P. GESSEL[1]

ABSTRACT

The effect of acid rain on forests and other non-agricultural ecosystems has been discussed by many writers in recent years. The 1977 Alberta Sulphur Gas Workshop was favoured with an address by Dr. Overrein of Norway, relative to the impacts of acidic precipitation over wide areas. A great deal of concern is being currently expressed about the effects of acidic precipitation on forests and waters of the northeastern United States and Canada.

This paper, rather than repeating these reviews, considers some of the problems encountered in forest ecosystem studies of acid rain effects. Problems of productivity evaluation and soil changes are discussed and data are presented.

The problem of assessing acid rain effects on forest productivity is one of quantification. It is difficult to detect small changes in growth rate and productivity because of the large variation in growth under natural conditions. Acid rain can result in increases or decreases in growth rate depending upon site nutrient status, and duration and rates of inputs. Increases in productivity may be related to sulphur or nitrogen deficient forest areas, and these are discussed.

Long-term productivity changes are theoretically possible because of cation depletion in some soils, and toxic aluminum accumulation in others. However, variations in nature caused even by differences in tree species occupying the site far exceed the effects of acid rain. Data from the states of Washington and Tennessee are presented to illustrate this. Work currently in progress at the University of Washington on the adaptation and nutrition of forest species in acid and high aluminum soils is reviewed, as is the role of sulphur in forest tree nutrition.

Finally, it is my contention that broadscale generalizations about acid rain effects on forests are not valid. We do need much more site specific information with regard to the nature of the inputs and the nutrient conditions of the site.

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ACID RAIN AND FOREST PRODUCTIVITY

S. P. GESSEL[1]

1. INTRODUCTION

The higher rainfall necessary to the successful growth of forests generally dictates that an acid leaching process is part of almost all forest ecosystems. The decomposition process in forests which converts forest debris, and initiates mineral cycles, releases organic, as well as inorganic acids, and these further acidify the system. Soil-forming processes characteristic of soils under most forests are governed by acid leaching. Numerous soil formation studies have examined soil as a function of age on sites such as receding glaciers or mud flows sequences. These clearly establish a relatively rapid increase in acidity.

Acidity is therefore normal to a forest. Under so-called natural conditions, we find an entire spectrum of acid conditions under forest vegetation. This is well recognized in forestry ecological literature and many species of plants have been described as indicators of certain soil pH's. Other species, especially some tree species, have been described as acidifying. For example, Norway spruce and European beech have developed reputations as acidifying species and recommendations against the use of these in pure stands have evolved. The effect of Kauri in New Zealand in causing extreme acidity in soils near the base of the individual stem is well documented as is also the case for certain eucalyptus species in Australia. Red alder, which grows over extensive areas in western North America acidifies the soil system more than Douglas fir.

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[1] Professor of Forest Soils, College of Forest Resources, University of Washington, Seattle. The author is indebted to Dr. Dale Johnson of Oak Ridge, Tennessee, and Dr. Dale W. Cole, College of Forest Resources, for considerable amount of data for this paper.

If increased acidity is a normal part of forest ecosystem development, why are we concerned with the effects of acid rain on the system? At least part of the answer lies in the fact that acid rain has secured a reputation as negatively impacting forest productivity. A number of reasons for the negative impact have been developed and these will be examined in the course of the discussion. However, I first propose to review some aspects of forest productivity.

2. FOREST PRODUCTIVITY

The subject matter of acid rain has been treated thoroughly in many reviews, and these are familiar to this symposium audience. However, the subject of forest productivity, and especially the problems of evaluating changes in productivity, may be less familiar. It therefore seems important to examine the nature of forest productivity, what factors in the productivity equation may be affected by acid rain, and problems of detecting productivity changes in natural forests.

In simplest terms, forest productivity can be defined as the capacity of the forest to produce, and parameters established to measure that production. As our forest lands are expected to produce many things for a variety of different users, a complete definition may have to take all of these into account. For example, some users expect the forest to produce water, some recreational experience, some deer or fish, some floral brush, and some wood. Each of these may have a different quantitative base for an expression of productivity. For this discussion, I will talk about wood productivity, but realize that uses frequently interact, and that acid rain could affect all uses differentially.

Forest productivity for wood is evaluated in a general way by the word "site," and in a specific way by volume or weight of wood produced per unit area. In the simplest form, we describe it as cubic meters per hectare per year of solid wood produced. Values of productivity differ widely when different forest areas of the world are compared but also widely within local forest areas. As an example, forest productivity within western Washington varies locally from about three to 30 cubic meters per hectare/year, or by a factor of at least ten. Comparisons of productivity from one forest area to another establishes even greater differences. These differences may or may not have been influenced by man.

The reasons for differences in forest productivity is a matter of considerable interest and much scientific inquiry in forestry literature. I will not attempt a review here, but use a simplified approach by considering forest productivity as a function of a number of parameters. These are climate, the soil system, the biological characteristics of the tree, the age of the tree or forest, and the management system. An evaluation of the effect of acid rain on forest productivity must take into account the effect on these productivity parameters. The soil system emerges as an important consideration, and we obviously must examine contributions of the soil to forest productivity and the effect of acid rain on these.

The soil functions in the life of forest trees as an anchoring medium for roots, a source of water and a source of essential elements, the characteristics of the soil which enhance its ability to encompass a vigorous and healthy root development generally improve the ability of the soil to supply water and essential elements. Although water supplying ability of forest soils has been deemed important in forest growth for a long time, nutrient supply has received attention only comparatively recently. Nitrogen and phosphorus are generally found to be elements which may be limiting forest growth in many forest areas of the world. However, under specific soil conditions deficiencies of any of the essential elements may affect forest productivity. The effect of acid rain on the ability of forest soil systems to supply essential elements will be the subject of much of this paper.

A few other points are in order with respect to acid rain and forests. Attempts to evaluate the effect of any changes in acidity of rain on a forest are complicated by at least two factors:

1. The acid rain occurs over substantial areas and it is, therefore, almost impossible to have adjacent control areas wihin the same environment. Movement outside that environment to establish control areas does have experimental hazards;
2. Statistically significant changes in forest growth are difficult to establish if they are small. The great variation in forest growth rate related to local stand conditions necessitates extensive sampling over a wide range of conditions.

As an example, we have established over 1 000 plots throughout Washington and Oregon to evaluate growth changes from nitrogen fertilization. We believe we can use growth changes as low as 8 to 10% as evidence of response by Douglas fir, but where local growth responses are more variable, as is the case with western hemlock, we are not able to state with certainty that there is a response even up to 12 years of growth records.

It is frequently difficult to detect changes in growth in forest trees resulting from major natural events. As an example, the May 1980 eruption of Mt. St. Helens was a total disaster for large areas of forests. An even larger forest area received deposition of airbourne materials from the eruption. A series of fertilizer installations received ash in amounts almost undetectable to about 6 to 8 cm. Examination after two years on plots over this range of ash deposition shows little differences in growth rates from the atmosheric inputs.

Finally, the death or dying of trees in a forest, changes in foliage color, or change in apparent tree vigor may be cited as evidence of acid rain damage. Unfortunately, these may also be caused by a wide number of other influences which affect forest trees. Carefully coordinated studies and observations to establish what is affecting forest trees are relatively rare in forestry but are very essential in order to separate fact from fiction about damage to trees from a large array of potentially injurious influences.

3. ACID RAIN AND FORESTS

The emergence of acid rain as a major concern with respect to forests comes from a possible accelerated leaching of cations from forest soils, and subsequent productivity loss (Engstrom et al. 1971). It thus appears that productivity changes from acid rain may result largely from potential changes in the soil system. There can be some direct effects on the tree itself, but the literature on this is not very large. This concern was the driving force for numerous empirical studies of acid rain effects on forest nutrient status in general and cation leaching in particular (Tamm et al. 1976, Cole and Johnson 1977, Cronan et al. 1978, Abrahamsen 1980a, Andersson et al. 1980).

Because of the negative implications of the term "acid rain," initial speculations about acid rain effects on forest productivity devoted little or no attention to concurrent sulfate and nitrate deposition on forests deficient in S or N (Jonsson and Sundberg 1972). Recently, it has been recognized that acid rain can cause increases, as well as decreases, in forest productivity (Abrahamsen 1980b, Cowling and Dochinger 1980). The net effect of acid rain on forest growth depends upon a number of site-specific factors, particularly nutrient status and amount of atmospheric acid input. In cases where cation nutrients are abundant and S or N are at deficiency levels, moderate inputs of acid rain will very likely cause increased forest growth. At the other extreme, acid rain in sufficient amounts will probably reduce productivity on sites with adequate N and S but deficient in cation nutrients. In either case, the costs and benefits of acid rain are highly dependent upon the quantities of nutrient capital and acid inputs involved (Johnson 1981).

It is also very important to consider that ions such as SO_4^{2-} and NO_3^- are already available in the ecosystem and H^+ is generated naturally by the plant community. Thus, the question is one of relating inputs to natural levels; e.g., does atmospheric H^+ input significantly add to or exceed natural H^+ production within the soil? Do the detrimental effects of H^+ deposition offset the benefits of NO_3^- deposition in an N-deficient ecosystem?

The greatest amount of information on acid rain and forest productivity concerns nutritional effects. Abrahamsen (1980b, p. 14), in his thorough review of the topic, states that, "Apart from possible direct effects of acid precipitation on forest trees, the effects on forest growth can be considered as a nutrition problem." Nonetheless, both speculation and some empirical evidence indicate that acid rain can have "direct" or non-nutritional effects on forests, also (e.g., Tamm and Cowling 1977). This discussion will consider both nutritional and non-nutritional effects, but the latter section is much shorter than the former, reflecting a relative lack of information and perhaps a general research need.

4. NUTRITIONAL EFFECTS

Acid rain, in the form of H_2SO_4 or HNO_3, is only part of a broad spectrum of pollutant inputs which can affect forest nutrition either positively or negatively (Cowling and Dochinger 1980). For any given site, evaluating the effects of acid rain in isolation from the frequently associated inputs of NH_4^+, for instance, would not only be unwise but totally impractical. However, the kinds and amounts of associated pollutant inputs vary considerably, and adequate discussion of total pollutant effects on forest nutrition is beyond the scope of this paper. Rather emphasis will be placed on overall forest productivity from acid rain. The paper will also include short sections on forest areas most sensitive to acid rain and how forest management activities may be used to ameliorate some of the deleterious effects of acid rain.

4.1 EFFECTS OF H^+ INPUTS

Deficiencies of H^+ (i.e., excessively alkaline soils) are virtually unknown in forests, but estimations of excessive or toxic levels of H^+ input must be based upon the natural H^+ production within forest ecosystems. Within forest soils, H^+ is produced by carbonic and organic acids, either of which can play a major role in cation leaching under natural conditions (McColl and Cole 1968, Johnson et al. 1977). Organic acids also leach from the canopies of some unpolluted subalpine and northern forest ecosystems, substantially reducing the pH of "clean" rain (5.65) passing through the forest canopy (Table 1). Oxidation of S, N, and P following litter decomposition also produces H^+, and a very significant mechanism of H^+ production in many forests is H^+ release by plant roots while taking up cations (Sollins et al. 1980, Andersson et al. 1980).

There are basically two ways to assess the roles of internal vs. atmospheric H^+ inputs to forest ecosystems. One approach involves a detailed assessment of H^+ production and consumption within the ecosystem, and generally indicates that atmospheric inputs comprise relatively small contributions to the total H^+ budget (Ulrich 1980, Sollins et al. 1980, Andersson et al. 1980). The other involves an input-output assessment only, where the net effects of atmospheric vs. internal H^+ inputs on cation nutrient export are considered (Ulrich 1980, Cronan et al. 1978, Cole and Johnson 1977).

Table 1. pH, SO_4^{2-}, HCO_3^-, Cl^-, color total cation, and cation-anion balance of precipitation and throughfall from Findley Lake, Washington and Petersburg, Alaska (Johnson 1975).

	pH	HCO_3^-	SO_4^{2-}	Cl^-	Color[1] Units	Σ cations	Σ cations[2] Σ anions
	----	----	----	eq/L	----	----	----
			Findley Lake, Washington				
Precipitation	5.6	66	35	<10	0	106	5
Throughfall	4.4	0	64	<10	44	116	52
			Petersburg, Alaska (Wadleigh Site)				
Precipitation	5.5	72	<10	25	0	56	-41
Throughfall	5.0	51	23	51	44	138	88

[1] Alpha-platinum standard.

[2] Positive values imply the presence of unmeasured anion, probably organic (Johnson et al. 1977).

While the latter approach is more integrative and direct, it does not distinguish between cation leaching and soil acidification. Although these processes are often referred to together, they differ in several important respects. Specifically, soils can be leached of cations without being acidified if the rate of weathering from primary minerals to exchange sites exceeds the leaching rate. On the other hand, soils can be acidified without being leached of cations if the anion of the acid is immobilized in the soil (Johnson and Cole 1977). Under these circumstances, both the incoming H^+ and associated anion (usually SO_4^{2-}) are retained in the soil, causing acidification but no net cation loss. An example of this situation is given in Table 2, where H_2SO_4 was applied to a forest soil which retained both SO_4^{2-} and H^+.

The effect of acid rain on soil cation leaching is highly dependent upon the mobility of the anion(s) associated with the acid (Johnson and Cole 1980). This is due to the requirement for charge balance in soil solution, a requirement that precludes the leaching of cations without associated mobile anions. In the case of SO_4^{2-}, adsorption to free ion and aluminum oxides can be a major factor restricting mobility in highly-weathered soils (Johnson 1980), whereas biological immobilization is more prevalent for NO_3- (Vitousek et al. 1979). Soils low in free Fe and Al or high in organic matter (the latter of which appears to block sulfate adsorption sites; Johnson et al. 1979, 1980) are therefore generally susceptible to leaching by H_2SO_4 (e.g., Cronan et al. 1978), whereas ecosystems rich in N (i.e., where biological immobilization of NO_3- may be minimal) are probably susceptible to leaching by HNO_3.

When cation leaching is accelerated by acid inputs under controlled irrigation experiments, Ca^{2+} and Mg^{2+} appear to be the most affected and K^+ the least affected (Abrahamsen 1980a, 1980b, Hovland et al. 1980, Ogner and Teigen, in press, Wood and

Table 2. Effects of H_2SO_4 irrigation on cation leaching and soil pH in a sulfate-adsorbing soil (from Johnson and Cole 1977)[1]

	Soil pH		Cation budget for 4 months following acid application	
Horizon	AT	CT	H^+	TC
			------ (eq/ha)	-----
Acid application	-	-	35,520	0
A (0-12 cm)	4.6	5.1	0.2	11,200
B (12-50 cm)	5.5	5.5	0.2	200

[1] AT = acid treated, CT = control, TC = $Ca^{2+} + Mg^{2+} + K^+ + Na^+$.

Borman 1976). To some extent, this may reflect the relative amounts of these cations on soil exchange sites, but the rate of increase in K^+ depletion seems to be consistently below that for Ca^{2+} or Mg^{2+} under acid irrigation as well (Abrahamsen 1980a; Ogner and Teigen, in press; Wood and Borman 1976). This relative lack of response in K^+ may be due to the greater plant requirements for K^+ as opposed to those for Ca^{2+} or Mg^{2+} and possibly also due to fixation of K^+ in 2:1 clays.

The effect of acid rain on cation nutrient availability will depend on the net effects of leaching vs. weathering (Abrahamsen 1980b, Ulrich et al. 1980). Weathering might be stimulated by additional H^+ input, offsetting the leaching of exchangeable cations to some extent. However, most acid irrigation studies (Abramhamsen 1980b) and one study under ambient acid input conditions (Ulrich et al. 1980) indicate a net decline in exchangeable cations with time.

Acid rain may indirectly affect the availability of N and P in forest soils, also. Under sufficiently acid conditions (generally $pH \leq 4.0$), soil Al is mobilized (Cronan and Schofield 1979, Ulrich et al. 1980), leading possibly to Al toxicity and immobilization of P (Abrahamsen 1980b). Tamm (1976) predicted short-term increases in N availability (due to decreased decomposition and microbiological N immobilization) and tree growth due to acid rain, but long-term declines in both N status and growth due to net N losses from the ecosystem. With regard to decomposition, empirical results have been variable. Some irrigation studies note decreased decomposition or CO_2 evolution with sulfuric acid inputs (Tamm et al. 1976, Bååth et al. 1980), whereas others show little or no effect (Abrahamsen 1980a, Roberts et al. 1980, Hovland et al. 1980). However, several independent studies show increased N availability at least during the initial stages of sulfuric acid input (Roberts et al. 1980, Abrahamsen 1980a, Ogner and Teigen, in press), and not surprisingly, this increased availability produces growth increases in situations where N is limiting (Tveite and Abrahamsen 1980a ,1980b, Tamm and Wiklander 1980). Whether this increase in N availability is due to changes in microbial activity or to the acid-catalyzed hydrolysis of labile soil N is unknown as yet, however, and deserves further investigation. In either event, the results of the Norwegian studies in which both N availability and nitrate leaching were stimulated by H_2SO_4 inputs strongly suggest that, contrary to earlier predictions that nitrification would be inhibited by acid inputs (Tamm 1976), nitrification can be stimulated by acid inputs. The positive response to nitrifiers to increased ammonium supplies appears to outweigh the negative effects of H^+ inputs on nitrifier activity in such cases. This definitely has negative long-term implications for forest N and cation status if nitrate production exceeds plant uptake, resulting in net ecosystem N and cation loss.

Ulrich et al. (1980) forecast negative long-term effects of acid rain on the nutrition of a *Fagus sylvatica* stand at the Solling site due to soil acidification and toxic accumulations of soluble Al. Resampling soils from the site over a 13-year period showed as predicted by Tamm (1976), significant accumulations of N-poor organic matter in the forest floor (which are thought to promote internal H^+ production as well as to tie up N) and very large increases in soluble Al. As with all field studies of ambient acid rain effects, no control sites were available to show to what extent these changes would have occurred without the influence of acid rain. Accumulations of N-poor organic matter in the forest floor have been noted during stand development in relatively unpolluted Douglas fir forests, for example (Turner 1975). Nonetheless, these findings deserve careful consideration because the only alternative to uncontrolled pre- and post-treatment assessments of this nature is to artifically add acid to the ecosystem, perhaps inducing effects that would not occur under ambient loadings (Bache 1980).

Johnson et al. (1981) present circumstantial evidence suggesting forest growth loss in the New Jersey pine barrens due to acid rain. That is, a decrease in the growth of pines (as indicated by tree ring analysis) beginning in the mid 1950's coincides closely with a decrease in stream pH. Because the soils are sandy, shallow, and very poorly buffered, the acid rain effect is quite possible although as yet unproven.

4.2 EFFECTS OF SO_4^{2-} INPUTS

Deficiencies of S were indicated in forests remote from pollutant inputs in eastern Australia (Humphreys et al. 1975) and the northwestern United States (Youngberg and Dyrness 1966, Will and Youngberg 1978). Humphreys et al. (1975) strongly suggest that pollutant inputs from power plants are beneficial in S_2-deficient Australian forests, particularly when the soils have little SO_4^{2-} adsorption capacity. Fertilization with S in such cases is very inefficient because SO_4^{2-} rapidly leaches away, necessitating continual refertilization to maintain adequate S supply. In these situations, the continual input of moderate amounts of atmospheric sulfur may be an ideal, if inadvertent, source of fertilizer.

At the other extreme, continual atmospheric S inputs may help alleviate sub-optimal sulfate availability in sulfate "fixing" soils, such as those of the tropics that are rich in hydrated Fe and Al oxides. Although adsorbed, water-insoluble sulfate is thought to be available to plants in the long run, the intensity or rate of supply to soil solution can be less than that required by plants, effecting an S limitation (Hasan et al. 1970).

It is also clear that fertilization with N, a common practice in many forested regions of the world, results in the rapid utilization of ecosystem S supplies, possibly leading to S limitations (Humphreys et al. 1975, Turner et al. 1980). In fact, it has been strongly suggested that forest N and S status must be evaluated together because of the closely related roles of these elements in the synthesis of protein (Kelly and Lambert 1972, Turner and Lambert 1980, Turner et al. 1980). In relatively unpolluted regions of the northwestern United States, there is evidence that lack of Douglas fir growth response to N is due to marginal S status (Turner et al. 1977). Thus, it seems evident that moderate amounts of acid rain as H_2SO_4 could especially benefit forests undergoing fertilization with N. In the United States, this currently involves a total of about 10^6 ha of forest lands, primarily in the northwest and southeast (Bengston 1979).

On the other hand, excessive inputs of S lead to large accumulations of SO_4^{2-} in both plant tissue and soils (Hesse 1957; Leaf 1968, Turner et al. 1980, Johnson et al. 1970, Johnson and Henderson 1979). Sulfur supplied in excess of that which can be utilized for protein synthesis, i.e., that present in excess of a set S:N ratio of 0.03 on a gram-atom basis, accumulates as SO_4^{2-} in plant tissue (Leaf 1968, Kelly and Lambert 1972, Turner and Lambert 1980). In fact, foliar SO_4^{2-} content has proven to be an excellent diagnostic criterion for plant S status (Leaf 1968, Kelly and Lambert 1972, Turner and Lambert 1980) and as an indicator of S pollution (Bieberdorf et al. 1958). For *Pinus radiata*, foliar SO_4-S levels less than 80 ppm indicate S deficiency; levels in excess of 400 ppm indicate excess SO_4^{2-} and probable N deficiency (Kelly and Lambert 1972). Toxic levels of SO_4^{2-} are not well defined (Turner and Lambert 1980). Linzon et al. (1979) point out that acute effects of excess S, such as during an SO_2 fumigation, must be considered separately from chronic effects in which S builds up in plants to threshold levels for injury, and furthermore, that such threshold levels may vary with site conditions.

Hesse (1957) and Turner et al. (1980) found that excess S not only accumulates as SO_4^{2-} in plant tissues but also cycles as SO_4^{2-} within forest ecosystems. This is not to say that individual SO_4^{2-} ions necessarily remain intact throughout uptake, return, and release by decomposition, but because large SO_4^{2-} components were found in every component and transfer process within the cycle, this possibility cannot be excluded. Why large amounts of SO_4 cycling occur under conditions of excess S input is not clear. There is no evidence to indicate that the cycling of SO_4^{2-} causes harm, and it may, in fact, help maintain charge balance in plant roots as they take up cations, precluding the necessity for H^+ release from roots to some extent.

By far the greatest sink for excess SO_4^{2-} in many forest ecosystems is the soil (Johnson et al. 1979, 1980). On Walker Branch Watershed, Tennessee, for instance, 48% of the total S input accumulates in the soil whereas only 13% accumulates in vegetation (Table 3; Shriner and Henderson 1978, Johnson and Henderson 1979). As discussed previously, sulfate accumulates in soils by inorganic adsorption to free Fe and Al oxides. The effects of this accumulation are beneficial in two ways: (1) prevention of cation leaching by a H_2SO_4 by immobilizing the sulfate anion; and (2) creation of new cation exchange sites (Wiklander 1980, Rajan 1978).

4.3 EFFECTS OF NO_3- INPUTS

Deficiencies of N are very common in forests throughout the world (Abrahamsen 1980b) and inputs of NO_3- (as well as NH^+ and other forms of N) are very likely to improve forest productivity in many cases. For instance, Wood and Borman (1976) found that additions of artificial acid rain containing NO_3- stimulated the growth and foliar N concentrations of white pine *(Pinus strobus)* seedlings in a greenhouse study. The authors

Table 3. Content and annual accumulation of S in soils and vegetation of Walker Branch Watershed (from Shriner and Henderson 1978).

Component	Content ($kg \cdot ha^{-1}$)	Accumulation ($kg \cdot ha^{-1} \cdot year^{-1}$)
Input = 18 $kg \cdot ha^{-1} \cdot year^{-1}$		
Vegetation	73	+2.3
Soil	1300	+8.6

assumed a fertilization effect by NO_3^- additions, but the results of Tveite and Abrahamsen (1980) and Ogner and Teigen (in press) suggest that accelerated N mineralization or reduced heterotrophic N uptake may have been a factor.

The benefits of NO_3^- deposition on forest N status may depend upon the species involved. Some tree species are better adapted to NH_4^+ than NO_3^- as a source of N; some species are better adapted to NO_3^-; and some appear to require both (Krajina et al. 1973, McFee and Stone 1968). It is also noteworthy that NO_3^- uptake does not require exudation of H^+ from tree roots as NH_4^+ uptake does (Van den Driessche 1978). Thus, it is conceivable that HNO_3 deposition could cause reductions in internal H^+ production.

Nearly all forest ecosystems for which nutrient budgets are available appear to accumulate NO_3^- as well as other forms of N (i.e., inputs > outputs; Abrahamsen 1980b). Because NO_3^- is very poorly adsorbed to most soils (Johnson and Cole 1980), this accumulation is probably due to biological uptake (although denitrification may be a factor). In some cases where N is particularly deficient, NO_3^- uptake may occur even within the forest canopy (Table 4 from Johnson 1975). The inhibiting effect of NO_3^- immobilization on the leaching potential of HNO_3 is the same as that of SO_4 immobilization on the leaching potential of H_2SO_4 even though the mechanisms of immobilization for those two anions are entirely different.

Because forest N requirements are relatively high compared to S, there are very few instances of excessive NO_3^- inputs except in fertilization and wastewater or sludge application studies. Even in these situations, however, it is often impossible to separate the effects of NO_3^- inputs from those of NH_4^+ or organic N inputs. In any case, a major negative impact of excessive N input (defined here as being in excess of the ability of biota to utilize it) is excessive nitrate and associated cation leaching (Overrein 1971, Breuer et al. 1979, Table 4. pH, SO_4^{2-}, and NO_3^- of precipitation, throughfall, and soil solution following a rain event on June 25-July 3, 1973 (Johnson, unpubl. data), and average annual fluxes of SO_4 and NO_3^- for 1973 to 1975 (Johnson 1975) at the Thompson Site, Washington.

Sampling level	pH	SO_4^{2-}	NO_3^-
	June 25-July 3, 1973		
	---------- µeq/L ----------------		
Precipitation	4.2	120	352
Throughfall	5.6	94	<5
Soil solution (50 cm)	6.3	35	<5
	Average annual fluxes ($eq \cdot ha^{-1} year^{-1}$)		
Precipitation		260	38
Throughfall		320	<1
Soil solution (50 cm)		390	<1

Hook and Kardos 1978, Cole and Scheiss 1980). Forest ecosystems with adequate or excessive amounts of N (e.g., N-fixing species) are probably very susceptible to HNO_3 leaching, as mentioned previously.

Biological utilization of atmospherically deposited NO_3^- may ultimately improve forest growth and N status to the point where other nutrients become limiting (possibly including S in some cases). While this can hardly be construed as a negative impact overall (since deficiencies in the most limiting nutrient, N, will have been overcome), it is a factor worthy of consideration, especially with respect to cation nutrients that may be concurrently depleted by acid rain-accelerated leaching. Indeed, there are indications that after an initial growth increase due to N, Mg became limiting and growth decreased following the cessation of H_2SO_4 irrigation in the Norway spruce experiment of the Norwegian SNSF Project (Tveite 1980, Abrahamsen 1980b). Further observations must be made before any final conclusions are drawn on the cause of the growth decline, however.

Excess N can accumulate in tree tissues (e.g., Turner 1977), but unlike S it apparently does so largely in organic forms (accumulations of NO_3^- and NH_4^+ in plants is usually less than 10-20% of total N; Epstein 1972).

5. NON-NUTRITIONAL EFFECTS

Tamm and Cowling (1977) list several possible effects acid rain might have on forest trees, including damage to cuticle structure, interference with guard cell functioning, direct poisoning of plant cells after acid diffusion through stomata or cuticle, decreased photosynthetic efficiancy, alteration of leaf or root exudation processes, interference with reproductive processes, deleterious interactions with other pollutants and environmental factors, increased susceptibility to drought and other environmental stresses, and alteration of symbiotic and host-parasite relationships. Of this list of possible effects, even though it is not complete in itself, only a small number have been addressed in empirical studies.

Seedling germination and growth have been both stimulated and inhibited in a variety of studies involving artificial H_2SO_4 irrigation (Lee and Weber 1979, Abrahamsen et al. 1976, Matziris and Nakos 1977). Abrahamsen (1980b) reviews these studies and concludes that pH has a moderate effect on seedling germination and gives an overall optimum value of 4.7. He also reviews studies of seedling establishment and suggests that this process is more sensitive to pH effects than germination. The readers are referred to that paper for details which will not be repeated here.

Jacobsen (1980) reviews the state of knowledge regarding the phytotoxicity of acid precipitation, and some highlights are worth repeating here. It appears that foliar tissue damage is due mainly to free H^+ rather than to other ionic constituents of acid rain. In general, damage does not occur to any large extent until pH reaches values of 4.0 or below, although this will vary with species, stage of plant development, duration and frequency of exposure, and a number of other environmental factors (Wood and Borman 1976, Evans et al. 1978, Jacobsen 1980). Deciduous leaves appear to be more sensitive to acid rain damage than coniferous leaves, and the most vulnerable stage of plant development appears to be just prior to maximum leaf enlargement (Jacobsen 1980, Evans et al. 1977). There is little empirical evidence that acid rain affects plant physiological processes, but the possibility remains real and studies are currently underway. Further research is also needed to determine the effects of leaf structure and wettability on susceptibility to acid rain damage (Jacobsen 1980).

Shriner and Cowling (1980) review the effects of acid rain on plant pathogens, and only a brief summary is presented here. Acid rain can have either positive or negative impacts upon plant diseases by affecting the microenvironment of infection courts on leaf surfaces. It can promote infection by eroding protective cuticular barriers, intefering with guard cell functioning, creating lesions through which pathogens can invade, and leaching spore-germination inhibitors from plant tissues. On the other hand, there is empirical evidence that sulfuric or nitric acid applications reduce the incidence of some diseases, apparently by creating unfavorably acidic conditions for the disease organisms themselves.

6. SITE SENSITIVITY TO ACID RAIN

In general, sensitive sites are considered to be those with a poor capacity to buffer the effects of acid rainfall in one or more of the ecosystem components. The criteria for sensitivity to leaching by sulfuric acid are very different from those criteria for nitric acid because of the differences between nitrate and sulfate anions. Sites sensitive to leaching by sulfuric acid include those with soils low in free Fe and Al oxides and clay content but high in pH and organic matter content, all of which relates to sulfate adsorption capacity (Johnson et al. 1980). On the other hand, sites sensitive to leaching by nitric acid include those with an abundance of N (i.e., little biological use for atmospheric NO_3- inputs).

Thus, a tropical forest rich in N-fixing species but growing on a highly weathered soil should be highly resistant to sulfuric acid leaching but relatively susceptible to nitric acid leaching. N-deficient forests on highly weathered soils should be resistant to both nitric and sulfuric acid leaching. Studies on sulfate and nitrate fluxes at Walker Branch Watershed, Tennessee, and Coweeta, North Carolina, indicate that this is the case. N-deficient Douglas fir forests on young glacial soils of the Pacific Northwest should be susceptible to sulfuric acid leaching but resistant to nitric acid leaching. Studies of sulfate and nitrate fluxes at the Thompson Site, Washington, and studies of sulfate fluxes at Haney Forest, British Columbia, verify this hypothesized pattern (Table 4). N-rich red alder forests on these soils should be susceptible to both nitric and sulfuric acid leaching, however.

New England forests on Spodosols appear to be relatively sensitive to both nitric and sulfuric acid leaching by anion mobility criteria, an unfortunate circumstance in view of the heavy inputs of these acids in that region (Table 4). Studies by Likens et al. (1977) and Martin (1979) have shown little or no nitrate retention at Hubbard-Brook and other forested watersheds of New Hampshire, and studies by Martin and Pierce (1980) and Likens et al. (1978) show that additional nitrate leaching is easily stimulated by harvesting in these ecosystems. At the same time, studies by Fisher et al. (1968) and Cronan et al. (1978) indicate that atmospheric sulfate inputs dominate stream and soil solution chemistry at Hubbard-Brook and the White Mountains of New Hampshire. Sulfate adsorption by Fe- and Al-rich B21r horizons of Spodosols at Hubbard-Brooke appears to be blocked by associated organic matter coatings (Johnson et al. 1980).

Soils depleted of bases will often carry vegetation lower in bases (e.g., conifers) or with lower productivity, both of which lead to a reduced buffering capacity for acid rain. At present, the most extensive sensitive areas are Scandinavian forests together with some Northern Europe, Canadian, and northeastern U. S. coniferous stands. Further, it could be suggested that there may be a more general problem throughout the world, but these affluent countries are the only ones who have studied it sufficiently to be able to recognize the problem. It is more likely a case of cold climates requiring higher quantities of energy and utilizing high sulfur fossil fuels to produce it.

The shorter growing season may also be one of the factors in making the ecosystems more sensitive to acid rain.

7. FOREST MANAGEMENT INTERACTIONS WITH ACID RAIN

Many forest management practices (i.e., harvesting, fertilization, changing species) have obvious and well demonstrated effects on forest fertility. Acid precipitation compounds these effects in some cases and offsets them in others. For example, harvesting results in the removal of nutrients in biomass, and in some cases, by causing accelerated nitrification and nitrate-cation leaching (Martin and Pierce 1980, Likens et al. 1978). Acid rain may help offset N and S losses in some cases and may compound cation losses in other cases. Following harvesting, decomposition and nutrient mineralization generally increase, but acid precipitation, reaching the litter layer directly without canopy buffering, may retard decomposition (Baath et al. 1980). Similarly, acid precipitation reaching litter layers may inhibit N fixation (Alexander 1980) following harvesting.

Fertilization obviously adds to the nutrient capital of the ecosystem, but it can result in the immobilization or loss of other nutrients as well. Nitrogen fertilization, by far the most common fertilizer practice, can cause nitrification and soil acidification if done in excess (e.g., Tamm and Popovic 1974). On the other hand, N-fertilization is known to immobilize free SO_4^{2-} in foliage, and it may improve the resistance of trees to direct effects of acid rain. Fertilization programs would be improved by considering atmospheric inputs and their implications to site fertility.

Conversion from deciduous to coniferous species, a common practice in many parts of the United States, may lessen the negative impacts of acid precipitation on forest nutrition because of the lower cation nutrient demands of conifers. Also, conifers are known to have an acidifying effect in themselves and are therefore less likely to be negatively affected by atmospheric acid inputs. On the other hand, acid precipitation may accelerate acidification processes in coniferous ecosystems.

Acid precipitation is a fact of life in most managed forests. Management plans should take into account potential effects coupled with the management interactions these inputs might have on forest nutrition. These effects are site-specific, however, and it is only possible to generalize on the basis of species, site conditions, and amount of inputs.

8. SUMMARY

The effects of acid rain on forest productivity have been thought of and researched primarily in the sense of a nutritional problem, probably because of the initial concerns for Ca^{2+} depletion in Scandinavian forests (Engstrom et al. 1971). Results to date have clearly shown that nutritional effects can be positive (at least initially) by the addition of S and N to forests deficient in these nutrients, and possibly also by the stimulation of a net increase in soil N mineralization. Although the fertilization effects of acid rain are totally inadvertent, they are no less real than very purposeful fertilization programs, and there is no scientifically justifiable reason for casting one in a negative light and one in a positive light. On the other hand, the possibilities that acid rain may cause forest growth reductions over time are also very real. Alleviation of N or S deficiencies will create greater demands for other nutrients. The cation leaching potential of acid rain may eventually be realized as soil SO_4^{2-} adsorption sites fill up and biological demand for NO_3^- is reduced, allowing greater mobility of these anions. The net result of these changes in nutrient flux and status could be the depletion of cations to deficiency levels, acidification of soils, concomitant solubilization of Al, and reduction in available P.

The accumulation and cycling of excess S is probably the least understood potential long-term effect of acid rain inputs. The plateau between S sufficiency and toxicity in forest ecosystems appears to be quite broad, since excess S often cycles without apparent harm as SO_4^{2-}. Inputs of S usually constitute a more significant increment to the natural sulfur flux within forest ecosystems than equivalent inputs of H^+ do to the natural flux of H^+. Therefore, it would appear that further emphasis ought to be given to the effects of the SO_4^{2-} component of acid rain. Similarly, further emphasis ought to be given to the effects of N inputs, because such inputs appear to be increasing (Abrahamsen 1980b) and N is the most commonly limiting nutrient in forest ecosystems.

Whether SO_4 accumulates to toxic levels or cations become limiting or some other factor such as host-parasite interactions or cell poisoning becomes critical first, excessive inputs of acid rain must ultimately lead to forest growth reduction. Surely, there has never been any question of this; the question is one of quantification not only of the "toxicity" thresholds but also of the deficiency-sufficiency thresholds. The entire problem of acid rain and forest productivity was unknowingly summed up very nicely by the 16th-century Swiss physician Paracelus: "All substances are poisons; there is none which is not a poison; the right dose differentiates a poison from a remedy."

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SESSION II

TERRESTRIAL

BIOMONITORING IN THE ATHABASCA OIL SANDS AREA OF ALBERTA: PROGRESS AND PITFALLS

P.A. Addison[1]

ABSTRACT

(An abstract was not submitted)

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BIOMONITORING IN THE ATHABASCA OIL SANDS AREA OF ALBERTA: PROGRESS AND PITFALLS

1. INTRODUCTION

Biomonitoring is a technique whereby biological samples are used both as indicators of pollution impingement and as a measure of air pollution impact. Obviously, the state of health of any organisms is the best measure of air pollution impact on that species. Biomonitoring also may utilize specific processes or formations of the ecosystem. As with an organism, a process such as decomposition of a plant community response may be the most effective way to assess pollutant impact to these ecosystem components.

Several plant groups, particularly mosses and lichens, have been shown to be sensitive to as well as very efficient in taking up and storing pollutants (Clough 1974; Richardson and Nieboer 1981). If the ecosystem in an area can provide a reliable and consistent measure of both impingement and impact of a specific pollutant or pollutant mixture, and if this is the objective, the expense of establishing and maintaining high technology monitoring instrumentation can be eliminated. This does not mean that air quality measurements will be out of date, quite the opposite. These types of measurements along with deposition studies will still be essential for pollution regulation and testing the reliability of biomonitoring techniques.

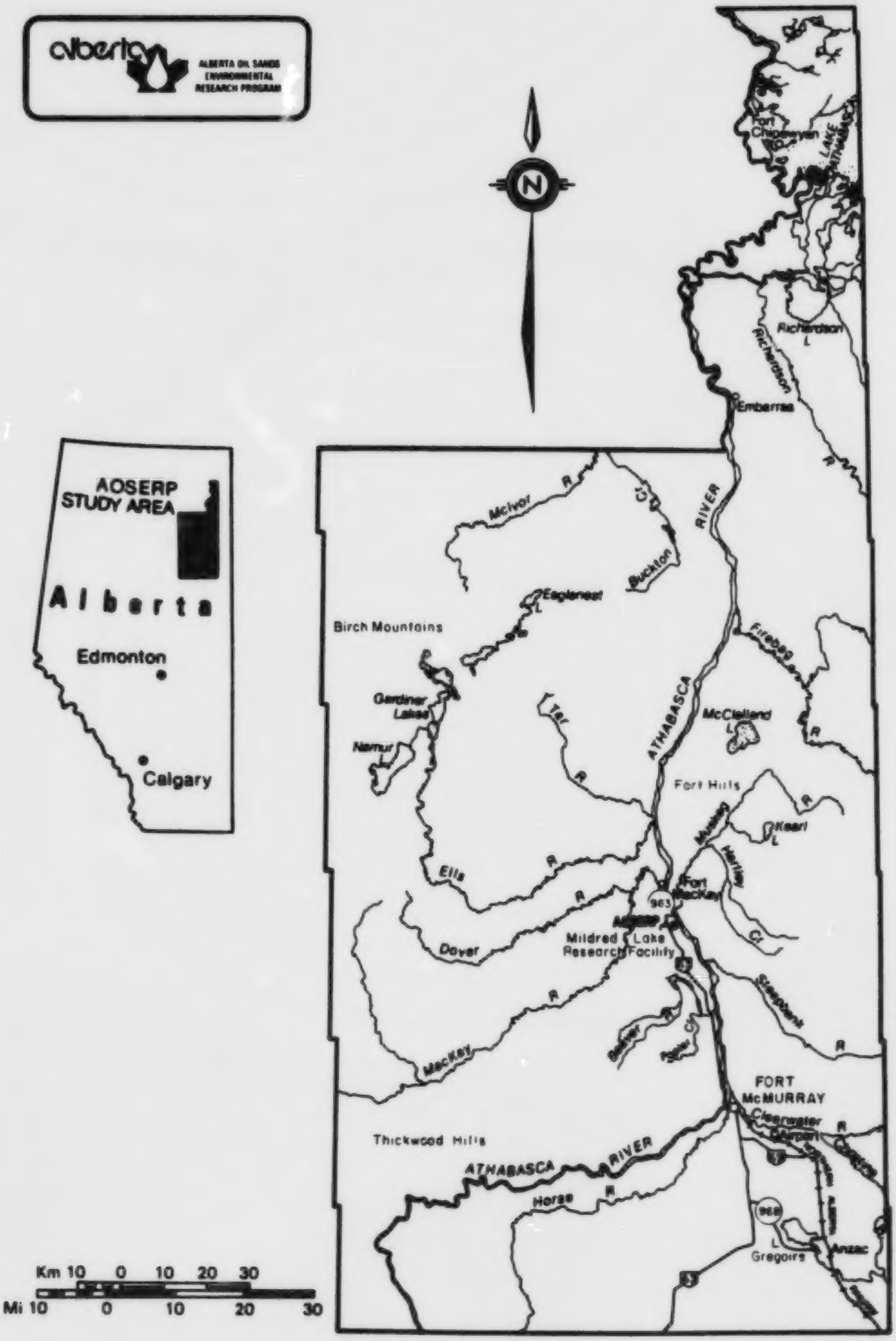
Several studies have attempted to use components of the terrestrial ecosystem as indicators of pollution deposition and impact in the Athabasca Oil Sands area. These studies have included the examination of particular groups of organisms such as insects (Hilchie and Ryan 1980) or lichens (Douglas and Skorepa 1976; Addison and Puckett

1980) as well as soils (Takyi and Nyborg 1977; Baker 1980) and vegetation (Addison 1980a; 1980b). The Athabasca Oil Sands area is northeastern Alberta is of particular interest in biomonitoring technique development owing to both the potential for long-range transport of air pollutants to the Province of Saskatchewan and the large amount of information on air quality and pollution deposition that has been generated by the Alberta Oil Sands Environmental Research Program.

This report describes biomonitoring techniques using soils and vegetation in the Athabasca Oil Sands area from 1975 to 1981. It is hoped that the information describing responses to air pollution in the vicinity of Suncor Inc., will serve as an indication of soil and plant monitors that have, and have not proved successful. This is important, particularly at this time when the Research Management Division of Alberta Environment is embarking on a biomonitoring research program. It is expected that with the history of biomonitoring in the area, the program concentrating on technique development may produce an effective biomonitoring system that can be used throughout much of this province and elsewhere.

1.1 STUDY AREA

All work was carried out in the study area as defined by the Alberta Oil Sands Environmental Research Program (Figure 1). The sites selected for detailed examination and manipulation were as close as possible to Suncor Inc., with a reference site at Fort MacKay, about 25 km north of the source (Figure 2). Sites included the five gradient sites (A to E), Fina Airstrip (F), Steepbank (G), Suncor Clearcut (H), Syncrude Turnoff (I), Mildred Lake Research Facility (J) and Fort MacKay (K). A substantial amount of time was spent in an attempt to select sites that were as similar as possible. Stand densities, types, and physical characteristics of soils as well as the composition of the vegetative components of these sites showed minor variation. It was imperative, however, to assume that the sites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Alberta
Edmonton
Calgary
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LAKE ATHABASCA
Richardson L
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Embarras
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RIVER
Buckton
Eaglenest L
Birch Mountains
Firebag R
Gardiner Lakes
Namur L
Tar R
ATHABASCA
McClelland L
Fort Hills
R
Kearl L
Muskeg
Hartley
Ells R
Fort MacKay
963
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AOSERP
Mildred Lake Research Facility
Cr
Dover
Steepbank R
R
Beaver R
Poplar Cr
MacKay
FORT McMURRAY
Clearwater R
Airport
Christina
Thickwood Hills
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Figure 1. Location of the Alberta Oil Sands Environmental Research Program study area.

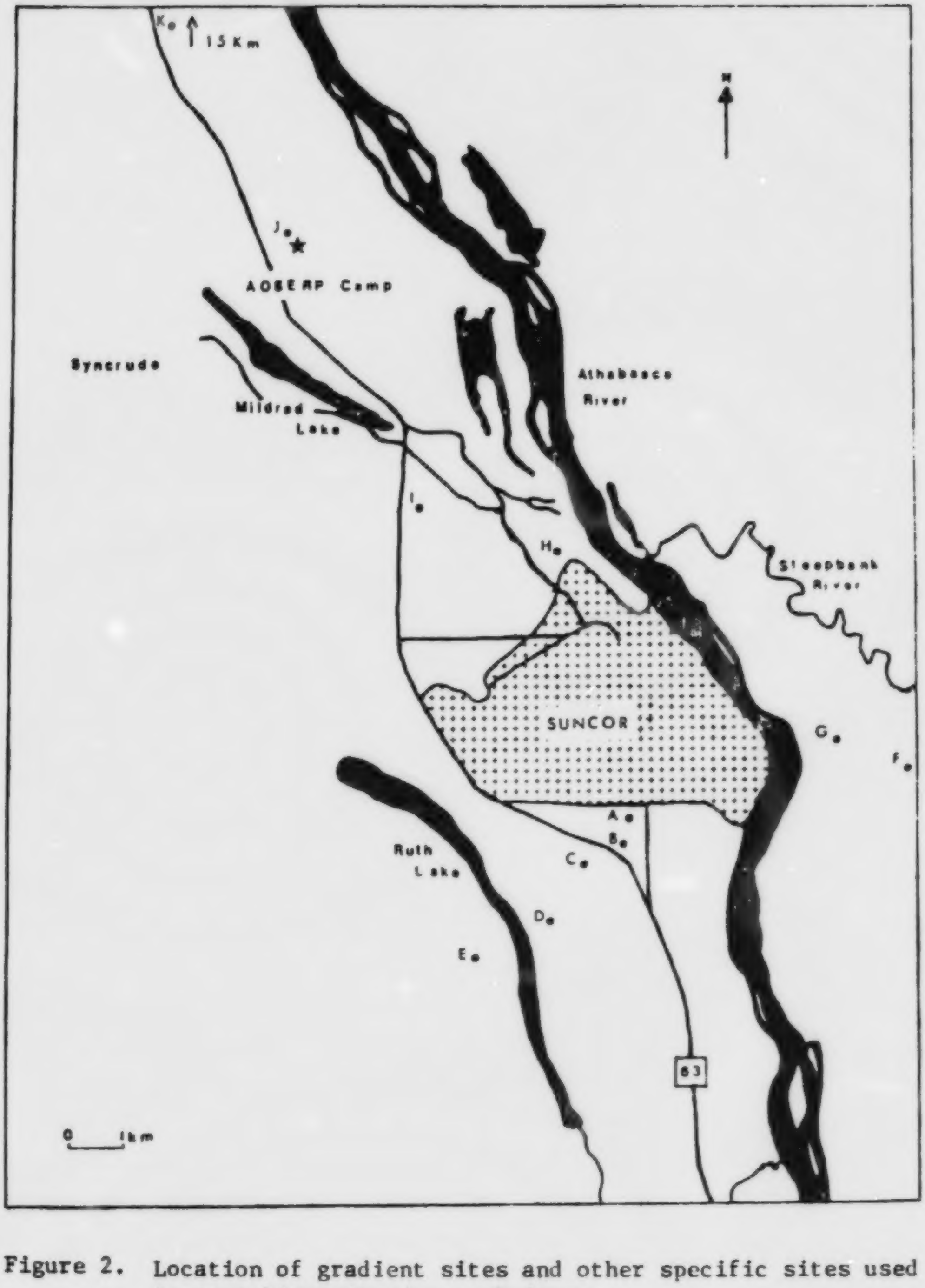
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Figure 2. Location of gradient sites and other specific sites used to test biomonitoring techniques.

were different and to quantify the differences that did exist. This was done to avoid the pitfall of making the unjustified and the theoretically unsound assumption that any two forest stands were identical.

2. METHODS AND MATERIALS

2.1 MEASUREMENT OF DEPOSITION

2.1.1 Physical Collectors

2.1.1.1 Precipitation. Three methods were used to monitor deposition of pollutants by both dry-fall and precipitation at sites A to E. In 1977, six cylindrical collectors (20 cm in diameter x 50 cm long) were placed in natural clearings at each site. Mineral oil was placed in each collector to prevent evaporation of the collected precipitation and the trapped material was collected monthly. In 1978, triplicate collectors were placed at the top of the canopy. In this case, a funnel was used to channel precipitation and particulates to a fibre-glass filter and then through a column of two ion exchange resins (one for cations and one for anions). The liquid was then trapped in a reservoir and the entire collector was retrieved after four months. In 1979, the same collector and locations used in 1978 were established with the exception that both the filter and the two exchange resins were eliminated. Samples were collected after four months and concentrated before analysis.

2.1.1.2 Sulphation. Huey plates, 10 cm in diameter, were placed, in duplicate, in three microenvironments (in the open, under jack pine and under white spruce) at sites A to E in the summer of 1977 and at sites A to G (excluding B), J and K from May 1978 to September 1979. Plates were mounted upside down to shield the reactive lead dioxide surface from precipitation. Plates were replaced and analyzed approximately monthly in the summer and every second month in winter.

Sulphation plates at a site close to Suncor Inc. (A) were placed in three different forest stands (jack pine, aspen, and black spruce). Duplicate plates were situated 3 m above the canopy, at the top of the canopy and at various heights (10, 5, 1.5, and 0.7 m). Plates were replaced on a 1 to 2 month interval.

2.1.2 Native Plants

Six species or species groups were sampled at sites A to E and analyzed for S, Al, Fe, P, and K. The species included jack pine (*Pinus banksiana* Lamb.), white spruce (*Picea glauca* (Moench) Voss), common labrador tea (*Ledum groenlandicum* Oeder), common bearberry (*Arctostaphylos uva-ursi* (L.) Spreng.), ground lichens (mainly *Pleurozium schreberi* (Brid.) Mitt.). These six species were selected because they demonstrated the greatest uptake of S close to the pollution source of the 15 species analyzed in 1976 (Addison, unpublished). These species also represented both dry and moist microenvironments. Five replicates were collected for each species. Pine and spruce samples consisted of 1-yr old material collected 7 to 10 m above ground, whereas other samples were of indeterminant age. Duplicate plant samples were passed through a 20 mesh screen and mineralized using an oxygen flask combustion technique (Chan 1975). Element analysis was carried out as described below.

2.1.3 Soils

Duplicate soil samples were collected from each horizon of the profile at each site. The soils were oven dried (105°C for 24 h) and digested using an aluminum block digester (Technicon Inc.) and teflon beakers. Samples (0.5 g) were predigested in 10 mL of 16N HNO_3 and 2 mL of 10N $HClO_4$ for 1.5 h at 70°C. Silica was then driven off with 20 mL of 29N HF at 150°C. The sample was taken to near dryness, dissolved into 1 mL of 12N HCl and brought to 50 mL with glass distilled water. Digests were analyzed for Al, Fe, and K with an atomic absorption spectrophotometer (Instrumentation Laboratories #251), P with an autoanalyzer, and S using a modified Johnson-Nishita method (Carson et al. 1972).

2.2 MEASUREMENT OF RESPONSE

2.2.1 Growth and Reproduction of Jack Pine

2.2.1.1 Basal Area. Radial increment growth of jack pine was determined at five sites (A, G, H, J, and K; Figure 2) by taking two cores from the south and west sides of trees (5 to 10) at each site. The increment for each of the previous 20 years was measured with an Addo-X Tree Ring Measuring Instrument, and the data from the two cores were averaged. Age (taken at 30 cm above the ground) of the trees sampled was also determined. Only cores that went through the centre of the tree were retained.

2.2.1.2 Shoot Length and Leaf Number. At a site close to the pollution source (Site A) and at Site J, about 10 km distant, five branches from the top one-third of each of five trees were collected. The length (distance between bud scale scars in mm) and the number of needles were determined for each of five age classes on each branch.

2.2.1.3 Seed Germination. The effect of air pollutants on jack pine seed viability was determined by collecting and testing seeds from mature (i.e., 35 year old) trees at sites A to E. Seed germination tests were carried out in the laboratory by placing 3 to 5 replicates of 50 seeds on moist filter paper at 20°C (day) and 16°C (night) fluctuating temperatures in the light. Germination was recorded after three weeks.

2.2.1.4 Biochemistry and Physiology. On several occasions during the summer of 1977, triplicate samples of both jack pine and white spruce branches were collected at sites A, C, and E and brought to the laboratory for biochemical and physiological investigation. The tissue was examined for phosphatase and malate dehydrogenase activities, chlorophyll/phaeophytin ratio, total sulphur content, net photosynthesis, and dark respiration. Methods followed were those of Malhotra and Khan (1979).

2.2.2 Plant Community

At each gradient site (A to E) in 1977, a 20 x 20 m plot was established and stand density and age as well as the cover and frequency of the lower stratum vascular plant species were determined. The lower stratum was quantified using 20 1 x 1 m quadrats that were randomly selected from a 20 x 20 matrix of the plot. The sample area represented 5% of the total and quadrat size was greater than the minimum sampling area required as defined by Cain and deCastro (1959). All quadrats were mapped so that future measurements of the site would be as close as possible to the first.

In 1979, these sites were re-examined and the cover of each species in the same quadrats was again estimated. Sites were subsequently compared with themselves and the change over time recorded.

2.2.3 Studies of Naturally Occurring Lichen

2.2.3.1 Condition and Element Content. Samples of *Evernia mesomorpha* and *Hypogymnia physodes* were collected from 69 locations in the vicinity of Suncor Inc. operations (Addison and Puckett 1980). These two species were selected because they were the most common corticolous lichens in the area and represented foliose and fruticose growth forms. Samples of both species were collected from the bark of *Picea mariana* (Mill.) BSP. For each site, only material in the best physical collection was collected. A qualitative estimate of thallus condition on a scale of 1 (least) to 5 (most luxuriant) was made on the samples of *E. mesomorpha* collected for analysis. No such estimate was attempted for *H. physodes* since changes in this lichen morphology and colouration were too subtle to quantify. Tissue samples were oven dried at 80°C to constant weight (24 h). No attempt was made to remove surface deposits on the lichens, but all remnants of the substrate were removed.

All lichen material was frozen in liquid nitrogen and ground to pass through a 60-mesh sieve. Approximately 0.1 g of material was mineralized using oxygen flask combustion and S was determined as above. Potassium was determined on the same samples by atomic absorption. Aluminum, titanium, and vanadium contents were determined on ground, non-ashed samples by instrumental neutron activation analysis.

2.2.3.2 Biochemical Condition. Samples of *E. mesomorpha* were collected in September from sites A, C, E, J, and K (Figure 2). Samples were almost dry at the time of collection in the field. They were brought to the laboratory and kept at -15°C in the dark in polyethylene bags until analysis of acid phosphatase, protein biosynthesis, and ^{14}C bicarbonate incorporation.

2.2.4 Studies of Lichen Transplants

2.2.4.1 Community. A branch lichen transplant study was initiated in 1976. Branches of black spruce were collected at Fort MacKay and relocated in five microsites at each of four locations (Sites H to K, Figure 2). Two branches were placed in a clearing and under jack pine, white and black spruce, and aspen at a height of 1.5 m. Quantification of the cover and frequency of the species groups present were accomplished using a 15 x 20 cm gray card and photographs. Each branch was marked and labelled and the lichens moistened slightly so that they were pliable. Spruce branches are oriented mainly on a plane and, hence, there was no difficulty in placing the quadrat below the branch. Lichens normally grow on the top and sides of branches and, hence, the entire stand was included in a photograph taken from directly above the branch.

Analysis of the photographs was done by projecting the transparency onto a 45 x 60 cm rear projection screen. The screen was divided into 100 units and the presence of each lichen species or species group was recorded for each unit. A correlation was made based on the average cover that each species had when it occurred in a unit.

Lichen community transplants were established at sites A to E in 1977 under spruce trees and the transplants (10 at each site) were quantified in the same manner as described. All transplants were re-examined each year between 1976 and 1980.

2.2.4.2 Element Content and Physiology. Pine branches bearing mainly *Evernia mesomorpha* were placed under jack pine trees. Six replicates were used at each site and material was collected from these transplants, brought into the laboratory and analyzed for total sulphur and available and total K^+ and Mg^{++}. Available K^+ and Mg^{++} was extracted by 1N HCl during shaking for 1 h. Analyses were done by atomic absorption spectrophotometry.

3. RESULTS AND DISCUSSION

3.1 DEPOSITION

3.1.1 Physical Collectors

3.1.1.1 Precipitation. Not one of the attempts to measure deposition through the collection of precipitation was successful. In 1977, damage to the collectors by bears was so extensive that, on several occasions, it was not possible to find a single collector intact after one month. The few samples that were collected were not analyzed since it would serve little purpose with the amount of missing data.

In 1978, collectors on the top of trees resolved the animal damage problem. In spite of much testing in the laboratory and a demonstrated capability of the exchange resins to trap and hold the elements of interest, it was not possible to rely on the results from this collector. After four months of exposure in the field, the resins showed some breakdown and released some of their trapped elements as well as some resin components.

In 1979, no pattern of pollutant deposition could be detected using samples of precipitation collected at the top of the forest canopy throughout the snow-free period (Addison 1980b). Several sites, however, had high levels of certain elements such as copper and sodium relative to the rest of the sites indicating contamination of the sample during processing. Further work is required on this technique before reliable results can be assured.

3.1.1.2 Sulphation Plates. Sulphation plates demonstrated that both distance and the type of canopy were important in determining the amount of SO_2 present at any location. At all sites, plates located in the open absorbed the greatest amount of SO_2, followed by those located under pine. In most cases, the amount of SO_2 absorbed by the plate under spruce was half to two-thirds that absorbed in the open (Table 1). The effect of canopy was significant ($p < 0.05$) in all months.

Table 1. Sulphur deposition ($mg \cdot m^{-2} \cdot d^{-1}$) in the vicinity of the Suncor Inc. operations in the Athabasca Oil Sands area in 1979.

Site	Distance (km) and Direction from Suncor		Open				Under Pine				Under Spruce			
			May	June	July	Aug	May	June	July	Aug	May	June	July	Aug
A	2.8	SSW	11.1	3.3	5.5	1.0	8.1	4.2	2.2	1.2	7.0	2.3	1.9	0.8
G	3.1	ESE	6.2	6.8	8.1	0.9	4.9	5.4	11.3	0.8	2.2	4.0	4.4	0.7
F	4.0	ESE	1.8	4.2	7.4	0.6	1.2	2.8	12.2	0.8	0.9	1.7	-	0.5
C	4.2	SSW	5.2	4.0	3.5	1.4	7.9	2.7	4.0	0.5	2.8	1.8	2.6	0.4
D	5.3	SSW	3.4	2.0	-	1.0	3.4	2.1	0.9	1.0	2.5	1.5	0.8	0.7
E	8.3	SSW	2.3	1.2	1.1	0.9	3.2	2.7	1.4	0.8	2.9	0.8	1.3	0.8
J	10.5	NW	0.3	1.3	1.5	1.4	0.9	1.4	1.8	1.3	0.7	1.3	0.9	0.9
K	23.7	NNW	0.4	0.3	1.2	1.5	0.5	0.5	0.9	1.0	0.1	0.1	0.7	0.9

Sulphur dioxide concentration appears to be highly dependent upon time of year, presumably as a result of changes in the prevailing wind direction. In general, the sites closest to the source had the greatest deposition at all times of year, and the two most distant sites represented background SO_2 levels for the area as a whole.

Sulphation plates placed at various heights in jack pine, black spruce, and aspen canopies substantiated the statement that the type of canopy is important to SO_2 deposition in forested areas (Figure 3). The open jack pine stand had a SO_2 deposition profile that would be expected in open areas with a sink of SO_2 at the ground surface. It mirrors the expected wind speed profile upon which it is at least partially dependent.

The other two profiles indicated the canopy structure. The black spruce stand became progressively more dense close to the surface whereas the aspen stand had a dense tree stratum separated from the high shrub stratum by about 3 m (3 to 6 m) of only the boles of the trees.

The importance of wind speed cannot be understated since it may be the primary factor causing the measured deposition profiles. Wind profiles are necessary before an assessment of the influence of the various plant species can be made. In spite of this limitation, it is apparent that SO_2 deposition to forested canopies of varying composition cannot be assumed to be the same.

3.1.2 Native Plants and Soils

Chemical analysis of selected plant species at sites A to E showed a substantial increase in S content at sites close to the pollution source (Table 2). Labrador tea and feathermoss had the highest S levels at all sites but the difference in S between sites A and E were similar for all species. Since there were substantial differences in S concentration between species at each site, no direct

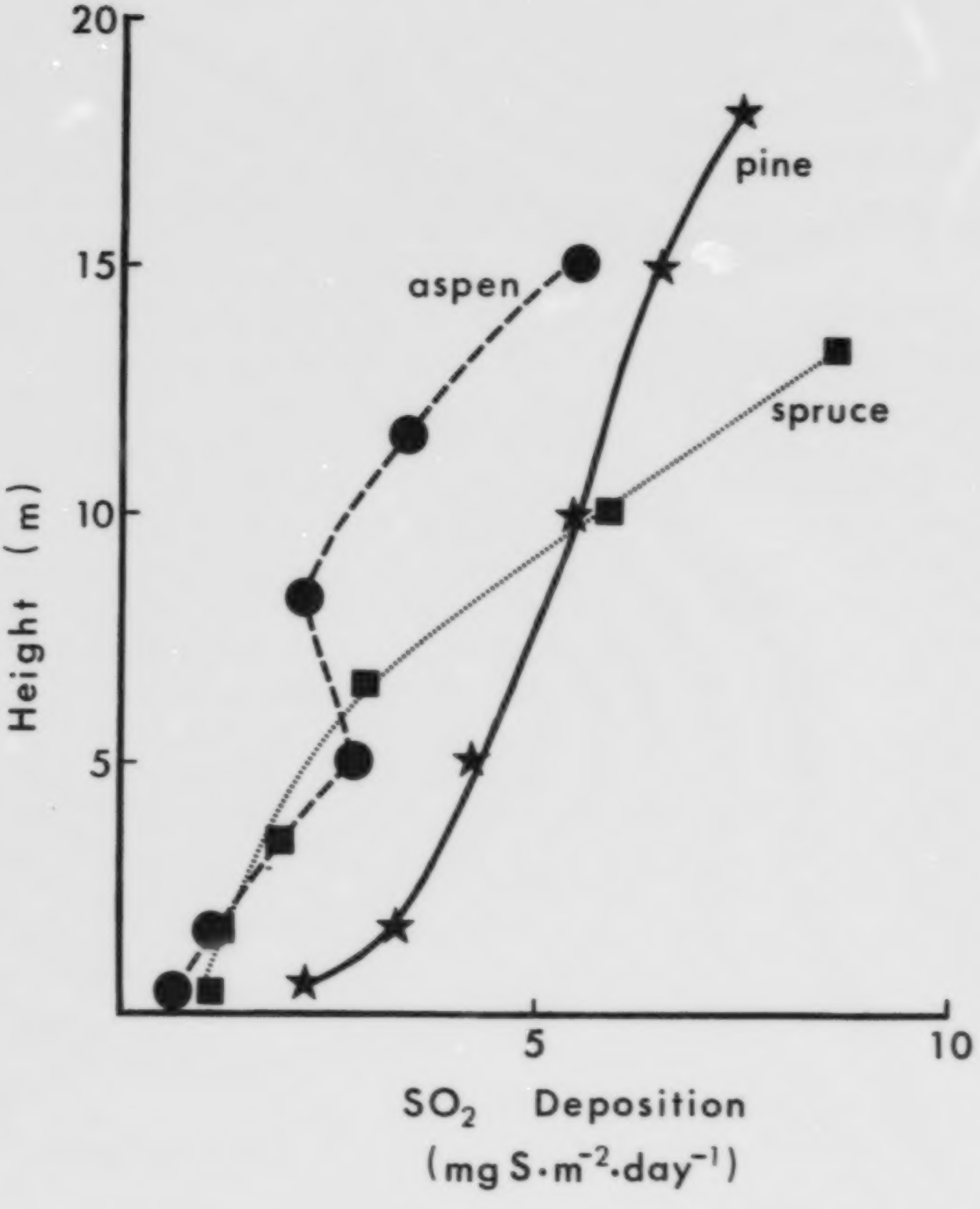

Figure 3. Profiles of SO_2 deposition to sulphation plates in three boreal forest stands in the Athabasca Oil Sands area. Values are averages of four measurements.

Table 2. Selected element content (ppm) of certain plant species at gradient sites in the vicinity of oil sands operations. Mean ± 95% confidence limits. Samples taken in 1977.

Site	Distance from Suncor (km)	Dry Phase			Moist Phase		
		Pinus banksiana	*Arctostaphylos uva-ursi*	Ground Lichens	*Picea glauca*	*Ledum groenlandicum*	Feather-moss
Sulphur							
A	2.8	1002 ± 48	796 ± 71	629 ± 38	918 ± 81	1409 ± 92	1289 ± 49
B	3.4	940 ± 60	601 ± 34	439 ± 51	718 ± 41	1288 ± 64	1434 ± 54
C	4.2	964 ± 28	677 ± 28	545 ± 27	735 ± 37	1146 ± 86	1419 ± 89
D	5.3	828 ± 30	559 ± 23	285 ± 25	691 ± 101	1180 ± 78	1195 ± 230
E	8.3	723 ± 40	423 ± 76	313 ± 74	496 ± 31	1054 ± 98	928 ± 89
Aluminum							
A	2.8	643 ± 60	397 ± 70	738 ± 369	303 ± 195	399 ± 54	2150 ± 1089
B	3.4	480 ± 83	549 ± 62	1051 ± 609	182 ± 46	473 ± 107	4772 ± 2162
C	4.2	626 ± 122	268 ± 54	620 ± 221	97 ± 31	203 ± 49	1294 ± 407
D	5.3	655 ± 100	196 ± 35	386 ± 181	253 ± 92	350 ± 76	2073 ± 262
E	8.3	668 ± 88	261 ± 54	392 ± 120	162 ± 21	276 ± 25	1528 ± 95
Iron							
A	2.8	191 ± 18	215 ± 31	293 ± 127	125 ± 34	248 ± 20	753 ± 373
B	3.4	199 ± 31	207 ± 32	417 ± 142	173 ± 26	475 ± 81	1093 ± 591
C	4.2	156 ± 30	162 ± 19	243 ± 73	102 ± 15	150 ± 24	715 ± 215
D	5.3	120 ± 25	190 ± 27	168 ± 61	300 ± 169	412 ± 78	2341 ± 338
E	8.3	331 ± 69	254 ± 49	241 ± 125	215 ± 31	338 ± 51	2165 ± 145
Phosphorus							
A	2.8	966 ± 129	1169 ± 145	382 ± 118	922 ± 90	1216 ± 94	494 ± 155
B	3.4	814 ± 105	848 ± 118	273 ± 86	1058 ± 102	1022 ± 79	754 ± 274
C	4.2	789 ± 80	960 ± 91	164 ± 41	919 ± 49	976 ± 125	620 ± 160
D	5.3	765 ± 48	821 ± 66	221 ± 41	763 ± 72	1061 ± 45	1060 ± 192
E	8.3	892 ± 19	958 ± 58	151 ± 30	1139 ± 80	1136 ± 113	1091 ± 56
Potassium							
A	2.8	3322 ± 432	4633 ± 231	489 ± 112	4199 ± 560	4063 ± 156	2093 ± 776
B	3.4	3186 ± 408	3616 ± 332	546 ± 227	3785 ± 430	3502 ± 236	3408 ± 1229
C	4.2	3556 ± 306	4691 ± 608	444 ± 122	3782 ± 228	4125 ± 509	2488 ± 714
D	5.3	3020 ± 429	4904 ± 77	398 ± 90	3011 ± 382	3988 ± 473	4111 ± 1228
E	8.3	3631 ± 289	4756 ± 359	321 ± 71	5115 ± 404	3439 ± 414	5675 ± 519

comparison could be made. Regressions were constructed for the S concentration of each species versus distance from Suncor Inc. and the Y intercept in each case was considered as maximum S content (100%). Regression coefficients were determined for relative S contents and this gave a measure of the decrease in S content with increasing distance.

Similar values were calculated for sulphation plates and for arboreal lichen S content (Table 3; Addison and Baker 1979).

Higher S levels close to the pollutant source did not appear to be related to soil S content and there was little difference among sites in the rhizophere (Ah, Ae, and Bm horizons; Table 4). The LFH horizon did show a distinct gradient in S either as a result of direct long-term deposition or because of addition by leaf-fall, or both.

Understory plant species in dry locations had a much greater increase in S with decreasing distance from the processing plant than did those related to the difference in stand density and the lushness of the lower stratum of the community. The dry sites were far more open than the moist ones and, hence, the pollutant could enter the stand and fumigate the ground vegetation much more readily. White spruce from moist sites on the other hand, had a greater rate of increase in S content than jack pine. In this case, both samples were collected well up the tree where SO_2 could easily impinge on the tissue. It is felt that the differences between these two species may be related to the resistance to entry of the gas imposed by the stomata.

3.2 MEASUREMENT OF RESPONSE

3.2.1 Growth and Reproduction of Jack Pine

3.2.1.1 Basal Area. There did not appear to be a relationship between the cross-sectional area increment and distance from the pollutant source (Table 5; Addison 1980b). There was actually greater growth in the last 10 years relative to the previous 10 years close to Suncor Inc. than at 10 km distance. Even though this form of self-standardization (comparing each tree's increment with itself before industrialization) can eliminate much of the site-induced variability, it appears that growth changes still need to be very large before they can be detected with any confidence.

Table 3. Regression coefficients of relative sulphur content versus distance from Suncor Inc. for selected plant species and sulphation plates (1977).

Material	Microsite Type	Microsite Location	Regression Coefficient
jack pine	dry	canopy	-4.5
bearberry	dry	ground	-6.5
ground lichens	dry	ground	-7.4
white spruce	moist	canopy	-6.3
labrador tea	moist	ground	-3.7
feathermoss	moist	ground	-5.1
sulphation plates	both	1.5 m	-8.2
arboreal lichens	dry	1.5 m	-9.6

Table 4. Total element content (ppm) of the primary soil horizons at the gradient sites in 1977. Values are averages of 2 to 4 samples.

Site	Distance from Suncor (km)	LFH	A Ah,Ae,Ahe	Bm	C
Sulphur					
A	2.8	634	207	35	87
B	3.4	-	91	15	5
C	4.2	498	35	9	9
D	5.3	128	108	44	33
E	8.3	68	13	25	33
Aluminum					
A	2.8	7300	8849	16364	11863
B	3.4	-	8223	18374	12434
C	4.2	7688	7348	10063	12841
D	5.3	4714	9773	18424	14271
E	8.3	6636	6709	14251	6401
Iron					
A	2.8	3718	3427	12240	7999
B	3.4	-	1875	8673	4157
C	4.2	2977	2530	6478	6422
D	5.3	1605	2473	13186	5686
E	8.3	2865	1983	11893	6326
Phosphorus					
A	2.8	956	246	339	111
B	3.4	-	417	565	297
C	4.2	878	320	623	310
D	5.3	541	102	262	93
E	8.3	1024	179	846	364
Potassium					
A	2.8	2162	4593	5892	5417
B	3.4	-	3571	6580	4703
C	4.2	2196	2661	2823	3932
D	5.3	1575	5337	5896	6387
E	8.3	1912	2627	4272	2996
Calcium					
A	2.8	732	261	147	142
B	3.4	-	216	105	83
C	4.2	543	113	77	103
D	5.3	199	192	124	147
E	8.3	571	80	120	85
Magnesium					
A	2.8	870	521	1024	764
B	3.4	-	414	1131	562
C	4.2	623	330	456	660
D	5.3	219	374	1140	749
E	8.3	800	259	868	467

Table 5. Ratio of wood cross-sectional area growth before versus after start-up of Suncor in the Athabasca Oil Sands area in 1966.

Site	Distance (km) and Direction from Suncor		Ratio of wood area 1968-77 ÷ 1957-67 (mean ± 95% confidence limits)
A	2.8	SSW	2.16 ± 1.26
H	3.0	N	1.15 ± 0.16
G	3.5	ESE	1.02 ± 0.50
F	4.0	ESE	1.62 ± 0.29
J	10.5	NW	1.48 ± 0.29

3.2.1.2 Shoot Length. Over the past 5 years, the jack pine at Site A produced significantly ($p < 0.01$) longer leaders of the lateral branches than did jack pine at Site J (Table 6; Addison 1980b). This observation concurs with the basal area growth measurements that showed over twice the radial growth at Site A ($435\ mm^2 \cdot yr^{-1}$) than at Site J ($215\ mm^2 \cdot yr^{-1}$). The differences seen in Table 6 are presumably a result of substantially better growing conditions at Site A that have not been significantly affected by the presence of air pollutants.

3.2.1.3 Leaf Number. The needle number of the most recent three age classes indicated that jack pine sampled at Site A produced more needles than did those at Site J (Table 6; Addison 1980b). This is consistent with both the leader length and basal area measurements that also showed greater growth at Site A than at Site J. In years 3 and 4, however, there were fewer needles per age class at Site A (Table 7), although the differences were not significant. It is thought that the reduction in needle number in years 3 and 4 may be a result of premature aging and abscission of leaves caused by air pollutants. Because so many natural factors may influence needle retention, no definite conclusion is possible. It should be noted, however, that even if premature needle drop does occur in the vicinity of Suncor, there is no evidence that it detrimentally affects plant growth and survival.

3.2.1.4 Seed Germination. The jack pine seed germination rate appeared to be reduced close to Suncor operations (Table 8; Addison 1980b). Site A had significantly ($p < 0.05$) lower germination rate than Site E, whereas the other sites were intermediate and were not significantly different from either A or E. There was also a significant correlation of seed germination with distance from the source ($p < 0.05$). Seed germination rate did not appear to be related to tree age (Table 8).

Table 6. Leader length of lateral branches of jack pine at Site A and at Mildred camp (J) in the Athabasca Oil Sands area. (mean and 95% confidence limits)

Age Class	Distance between Bud Scale Scars (cm)	
	Site A	Mildred J
Current	21.2 ± 2.2	15.8 ± 1.4[a]
1 year	24.0 ± 2.5	19.3 ± 2.2
2 year	23.4 ± 2.2	17.5 ± 1.9
3 year	27.6 ± 2.5	17.9 ± 1.6
4 year	25.4 ± 2.9	21.2 ± 1.9

[a] There are significant ($p < 0.05$) differences between sites for each age class.

Table 7. Number of needles per age class on the lateral branches of jack pine at Site A and Mildred (J) in the Athabasca Oil Sands area (mean ± 95% confidence limits).

Age Class	Number of needles		
	Site A	Mildred J	Significance
Current	115 ± 10	104 ± 8	NS
1 year	119 ± 11	100 ± 9	0.05
2 year	132 ± 13	93 ± 8	0.001
3 year	58 ± 22	63 ± 13	NS
4 year	14 ± 10	22 ± 10	NS

Table 8. Jack pine seed viability of trees from the gradient sites in the Athabasca Oil Sands area.

Site	Distance (km) from Suncor	Tree Age (y)	Seed Germination (%)
A	2.8	54.6	81.5[a]
B	3.4	33.6	89.4
C	4.2	29.1	90.9
D	5.3	40.0	94.2
E	8.3	42.0	95.8

[a] Lines join means that are not significantly different ($p < 0.05$) in a Student-Newman-Keuls test.

3.2.1.5 Biochemistry and Physiology. No significant differences in any of the metabolic responses measured were observed among the sites sampled. This may be owing to either the low concentrations of SO_2 experienced in these areas or the ability of spruce and pine to recover their metabolic functions between pollutant episodes. The concentrations of S in tissue (Table 2) were in the normal range for these species and it is felt that this, along with the plant's capability to detoxify the toxic species of sulphur (conversion of HSO_3^- and $SO_3^=$ to $SO_4^=$), that is responsible for the lack of response (Malhotra and Khan 1980). It should be pointed out that several of the biochemical and physiological responses measured here have been used to detect air pollution injury to plants near Flin Flon, Manitoba (Malhotra and Khan unpublished). This pollution source has been operating for a considerably longer period of time and releases both greater amounts of SO_2 and more persistent pollutants (heavy metals; particularly zinc) than oil sands operations.

3.2.2 Plant Community

The jack pine stands at the gradient sites (A to E) were selected because of their similarity. In spite of this, in 1977, there was considerable variability in species composition and cover of the lower stratum plants (Table 9). This variability did not appear to be related to either gaseous pollutant deposition (Table 1) or distance from Suncor Inc. The community structure and composition therefore, provided no evidence that the Suncor processing plant was having an effect on jack pine stands in the immediate vicinity of oil sands operations (i.e. < 8.3 km).

Measurements of the same sites in 1979 permitted direct comparison of each site with itself over a two year period. Changes in the stands could not be related to pollutants. It is thought that some of the changes in cover (Sorenson's index) at these sites were as a result of error in the placement of quadrats during repetitive

Table 9. Association table of cover values of the vascular plants in the lower strata of jack pine stands (A to E) in the Athabasca Oil Sands area (July 1977).

Species	Sites				
	E	D	A	C	B
Trees					
Picea glauca	0.03				
Pinus banksiana	0.03		0.03		
Populus tremuloides	1.45	0.35	0.05		
Shrubs					
Alnus crispa		8.50	0.13	8.20	
Amelanchier alnifolia			0.08		0.45
Prunus virginiana			0.05	4.13	
Rosa acicularis			0.08		
Ledum groenlandicum	0.30	2.08			
Vaccinium myrtilloides	6.13	9.78	11.70	7.05	2.55
Ground Shrubs					
Arctostaphylos uva-ursi	0.85	2.05	12.95	14.15	27.40
Vaccinium vitis-idaea var. *minus*	2.93	10.48	1.23	1.98	2.45
Linnaea borealis var. *americana*		0.75	0.50	0.50	0.85
Herbs and Grasses					
Unidentified Grass	0.53	0.50	0.53	0.53	0.60
Lilium philadelphicum var. *andinum*		0.18			
Maianthemum canadense	0.55	0.98	0.95	0.28	0.50
Comandra pallida	0.03	0.05	0.60	0.58	0.50
Geocaulon lividum	0.03				
Potentilla tridentata		0.13	0.28		
Viola nephrophila			0.03		0.05
Epilobium angustifolium	0.03	0.13		0.35	0.33
Aralia nudicaulis				1.28	
Cornus canadensis	0.53	1.80	0.18		
Pyrola secunda					0.05
Apocynum androsaemifolumi				0.03	
Mertensia paniculata				0.03	
Melampyrum lineare	0.23	0.23	0.10	0.18	0.18
Campanula rotundifolia			0.03	0.03	
Solidago decumbens				0.03	0.10
Pteridophyte					
Lycopodium complanatum		0.03		0.98	2.70
Total Cover					
Vascular Plants	13.65	38.02	29.50	40.31	38.71
Lichens	76.90	36.55	50.28	50.63	33.03
Mosses				0.25	0.05
Stand Density (stems/ha)	100	175	150	75	400

sampling. Individual quadrats were mapped but not permanently marked and, hence, errors in repositioning may have been responsible for some of the changes seen in Table 10. In addition, the amount of natural change that goes on at these sites is unknown.

Table 10. Similarity in Sorenson's index between 1977 and 1979 sampling times of jack pine stands A to E .

Site	Distance from Suncor (km)	Percent Similarity
A	2.8	88.4
B	3.4	-
C	4.2	83.6
D	5.3	85.3
E	8.3	84.5

3.2.3 Studies of Naturally Occurring Lichens

3.2.3.1 Condition and Element Content. Detailed results and discussion of the survey of lichens in the vicinity of Suncor Inc. have been reported elsewhere (Addison and Puckett 1980). The conclusions from this study indicated that: (1) the pattern of element deposition measured by lichen thallus concentration appeared to be related to the distribution pattern of elements as measured by physical and chemical methods; (2) the accumulation of elements by *Evernia mesomorpha* and *Hypogymnia physodes* could be related to both gaseous and particulate emissions from industrial sources and to localized windblown dust components; (3) a single collection of lichen material can replace traditional physical monitoring methods in locations where only relative deposition estimates of pollutants are required. The use of lichens in this manner also permits a measure of biological response that can be partially related to the content of specific elements in the thallus.

3.2.3.2 Biochemical Condition. No pattern that could be related to pollutants was observed in any of the metabolic processes examined (Table 11). Only the healthiest material from each site was used in the analyses and, therefore, it appears that the lichens that do exist close to the pollutant source are metabolically active. It is felt that impact to lichens occurs on an event basis when environmental conditions and pollutant levels interact to damage parts of the thallus. This hypothesis would resolve the apparent inconsistency between the metabolic and the field survey and transplant studies.

3.2.4 Studies of Lichen Transplants

3.2.4.1 Community. Lichen community response to air pollutants characteristic of oil sands operations, has been demonstrated by

Table 11. Metabolic activity of *Evernia mesomorpha* from sites in the Athabasca Oil Sands area. Values are means of three replicates ± standard deviation.

Site	Distance from Suncor (km)	Acid Phosphatase units/g dry wt	^{14}C incorporation 10^5 cpm/g dry wt	Protein Biosynthesis 10^5 cmp/g dry wt
A	2.8	1.7 ± 0.2	70.9 ± 2.9	13.3 ± 1.5
C	4.2	3.1 ± 0.2	55.7 ± 4.1	22.9 ± 0.9
E	8.3	1.8 ± 0.3	62.6 ± 6.2	17.3 ± 3.6
J	10.5	-	-	15.0 ± 3.0
K	23.7	-	-	13.9 ± 3.3

Addison (1980b). Response of transplanted lichens in the immediate vicinity of Suncor appeared to be the result of a complex of factors that include several pollutants as well as natural environmental factors. The importance of several factors in lichen response was demonstrated by Addison and Puckett (1980). Since changes in lichen condition of transplants were consistent with changes occurring on non-transplanted branches in areas of low or negligible pollutant deposition, the concern that small changes in microenvironment may dramatically affect lichen community composition and cover on a short-term basis appears unfounded.

3.2.4.2 Element Content and Physiology. Available to total ratios of K and Mg in transplanted *Evernia mesomorpha* appeared to be unrelated to air pollution (Addison 1980b). Variability of all measurements was great and it is clear that, in its present form, the introduction of lichen material for detailed examination of sulphur uptake or changes in physiological condition is inadequate as a biomonitoring tool. The technique, however, may be effective if more meaningful biological measurements are made and greater replication is ensured.

4. BIOMONITORING APPROACH

To date, our approach has been to work with well-defined, permanently marked and well-documented sites. The advantages of this approach are as follows:

1. It permits simultaneous assessment of numerous factors that may respond to pollutants. This results in greater reliability as it substantially reduces the possibility of a chance occurrence being interpreted as a meaningful response.
2. It permits the interpretation of one factor through the use of others. For example, a discussion on the exposure of a target organism in a forest without a measure of stand type and density would be meaningless, as would a discussion of plant pollutant content without soils analyses and physical measurements of pollutant deposition.
3. It reduces the natural variability that has to be dealt with in all ecosystems by allowing measurements of the same site over time.
4. It permits the establishment of a system that takes into consideration different types and rates of response. Biomonitoring, if it is to be used as a method to provide early warning of pollutant injury to the forest, must use a combination of techniques of differing sensitivities with known relationships between them so that both questions, What has happened? and What will happen?, can be answered.
5. It permits comparison of different types of responses and allows testing of the reliability and reproducibility of specific techniques.

The approach, however, is not without disadvantages. Only a small number of sites (< 30) can be handled since the technique is labour intensive. Sites must also be representative of the area. This is a particularly difficult requirement to satisfy in heterogeneous areas. A team approach which is often difficult to maintain is essential owing to the multidisciplinary nature of the work.

In general, this approach when applied to the Athabasca Oil Sands area of Alberta met with mixed success. It was possible to demonstrate that pollutants characteristic of oil sands operations were not distributed evenly. Distinct gradients in soil LFH horizon, native plant element content, and sulphation plates were observed in the vicinity of Suncor Inc. It is expected that precipitation measures would also show the same pattern if it were not for the technical problems encountered.

Demonstration of plant response to the deposited pollutants was much more difficult. Long-term measures such as vascular plant community change, soil nutrient change, and tree growth could not be related to pollutant deposition. Some plant responses such as lichen condition and pollutant content, jack pine seed germination and lichen community change appeared to be influenced by Suncor, but the magnitude of response is not great enough to be of alarm. Physiological responses of vascular plants and lichens that were expected to be very sensitive were far too variable to be useful without further refinement.

Many other biomonitoring techniques in a wide variety of disciplines warrant examination. Support of both government and industry proposed for the next few years shall provide biological tools for the detection of airborne pollutant effects on terrestrial ecosystems.

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AN EVALUATION OF QUANTITATIVE APPROACHES TO SOIL SAMPLING AND SOIL CLASSIFICATION FOR THE CHARACTERIZATION OF ENVIRONMENTAL IMPACT

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ABSTRACT

(An abstract was not submitted)

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1. INTRODUCTION

Soil is a primary component of all terrestrial ecosystems. The influence of soil quality on plant growth, reproduction and survival is undisputed. In addition soils influence water quality, patterns of local and regional hydrology and animals and human health. It is by reason of these roles that the modification of soil properties has become a critical issue in nearly all environmental monitoring programs.

The problems associated with monitoring soil changes or defining environmental impact on soil quality stem from two causes: first, it is difficult to select which property or groups of properties best represent the indicator of change or impact; secondly, all soil properties are spatially variable - they change minutely or greatly with distance - and can therefore be characterized only by statistical measures.

This paper deals only with the second aspect: If soils are variable, how can measurements be taken to calculate real changes or actual conditions? A summary of soil variability and its statistical representation is followed by a detailed discussion of several sampling procedures. Soil classification is shown to be a method whereby total variability can be partitioned by traditional survey methods or by "critical value dissection". Finally, the use of classification and sampling approaches are compared.

The reasoning underlying this paper is simple. Environmental impact on soils due to acid deposition or other factors, is best expressed quantitatively. If the detection of impact must await large, qualitative changes in soil properties or vegetation, perceivable by casual human observation, the damage will be extremely costly to repair. The application of quantitative methods to soil survey, soil sampling, soil classification and environmental impact assessment is a prerequisite to preventing soil deterioration and undue reclamation cost.

2. SOIL VARIABILITY

The soil is a continuously varying material and measurements of any one property made at different points will differ - some more, some less. There are spatial variations which may result from natural causes, such as sharp changes in vegetation or parent material, or from man-made variation. Total sulphur, for example, may vary widely across an area because of the impingement of a sulphur dioxide plume or be the result of wind-blown, elemental sulphur. Soil properties also vary among horizons of a given location. Vast variation may occur event within a particular horizon (Ball and Williams 1968, Petersen and Calvin 1965).

As long as there are large, consistent differences in critical soil properties between easily recognized soil types and soil horizons, a general description of soil class and a simple field sampling program will suffice for broad-ranging recommendations. However, when the critical soil properties change over very short distances or values fluctuate widely about an average, it is necessary to devise methods of measurement and prediction that account for fine differences and wide statistical dispersion.

The extent of soil variability is rarely recognized, but "ignoring its occurrence and its importance will not make it disappear" (Miller et al. 1980). Each soil property has a different amount and pattern of variability in relation to each soil landscape and management regime.

The data in Table 1 show how selected properties can vary over both large and small areas. The increase in variability with increasing sampling area is generally accepted but little studied (Beckett and Webster 1971). A more specific study done on soil pH shows the same pattern of increasing variance with increased distance (Figure 1).

In both cases (Table 1 and Figure 1) much of the variability in soil properties across a soil-landscape complex is already present within a few meters. Although it is difficult to imagine that soil cores taken from the same square meter are not extremely similar, there is substantial evidence to suggest the contrary (Ball and Williams 1968, Beckett and Webster 1971, Webster 1979). If decisions pertaining

Table 1. Topsoil coefficients of variation for increasing samplinh areas (Beckett and Webster 1971).

	Within field						More than one field	Between field component
	≤1 m^2		0.01 ha		one field			
	range	average	range	average	range	average	range	
Av. K	11-40	30	11-112	35	21-142	70	35-125	40
Av. P	7-45	30	13-121	40	11-131	45	35-320	55
Ca				10-40	20-260	30	95	35
Mg		10-20		10-20	15-71	45	25-65	35
Na					20	-	-	-
N OM					-	25-30	30-55	25
Texture		-		-	-	-	-	10

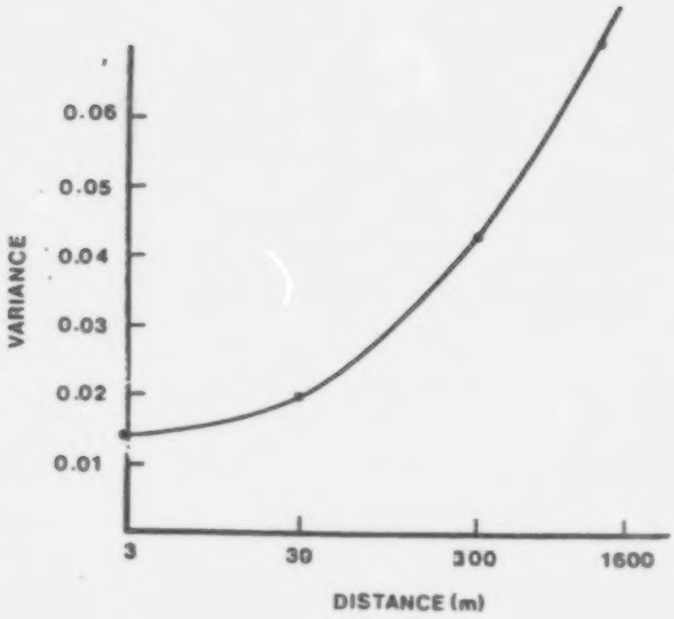

Figure 1. Graph of variance in pH with varying distance (Webster 1979).

to environmental impact are based on field sampling programs (Alberta Environment 1980), a measurement and interpretation of spatial variability for critical soil properties is essential.

3. STATISTICAL CONCEPTS IN SOIL SAMPLING

Soils are no different than any other variable material. Data which is gathered by the sampling can be summarized like those from any other set of individuals. Thus the mean ($\bar{X}$) and variance (s^2) are terms used to express the central position and dispersion in the sample. From these statistics one can calculate other items which are important in quantifying changes in material which has a high degree of variability. Standard error ($s_{\bar{x}}$) and confidence limits (CL) are two such statistics and are discussed later in this paper. Thornburn and Liu (1965) have an excellent discussion of individual statistics and general mathematical distributions as they are most appropriately applied to soils.

It is important to remember that statistics (items derived from sample measurements) are used to estimate the corresponding parameters in the total population. For this reason , they are subject to various sources of error, some of which can influence decisions in the quantitative assessment of environmental impact.

There are two kinds of error which may prevent the soil scientist from obtaining an accurage (i.e., close to the true value) estimate of the population location and spread. The first is systematic error, or bias, and results from a faulty selection of sampled individuals, poor measurement technique or bad instrumentation. Among soil scientists bias due to method of sampling is the most subtle and prevalent form. It commonly arises when the soil surveyor gives a greater representation to a soil-landscape unit in the sample than that which exists in the population (Miller et al. 1980, Mapping Systems Working Group 1981). The only remedy to systematic error resulting from a biased selection of sampled individuals is to ensure that the sample collection is random at some point in the procedure. This means that all points or areas in the population of interest have an equal chance to be observed (Arnold 1979).

The second kind of error is termed sampling error. This error arises from the inevitable differences between individuals included in the sample and those excluded. As a result sample estimates differ more or less from the true population values. In view of the fact that it is unavoidable, sampling error is accounted for by expressing it as the "standard deviation of the mean", or more simply "standard error".

The standard error is said to measure the precision obtained in a survey (Webster 1979). Precision is the clustering (or dispersion) of sample values about their own mean. The standard error can also be used to determine the confidence limits or accuracy of a survey. Accuracy refers to the success of estimating the true value of a population parameter. In the case of confidence limits of the mean, we may wish to determine the range within which the true population mean lies to a desired degree of confidence.

Since sampling error and, consequently, standard error, are most simply reduced by increasing sample size (Cochran 1977), an excellent estimate of the mean of any population size is obtained by taking multitudinous samples. For example, if we wish to know the sulphur content of a given area in order to know whether it has changed at a later time, we can estimate the mean content to nearly any degree of precision by taking enough samples. But if sulphur contents are highly variable then the sample size can be prohibitively large. Figure 2 shows the sample size increase necessary for differing levels of variability (expressed as coefficient of variation). It follows then that a decrease in variability will yield equally precise estimations at much smaller sample sizes. Soil sampling procedures and soil classification methods are expressly designed to reduce variability.

Accuracy, the closeness of the sample estimate to the true population mean, may be lost because of bias as well as a lack in precision (Freese 1981). An increase in sample size or a decrease in variability can yield a decrease in standard error and a concomitant increase in accuracy only if there is no bias.

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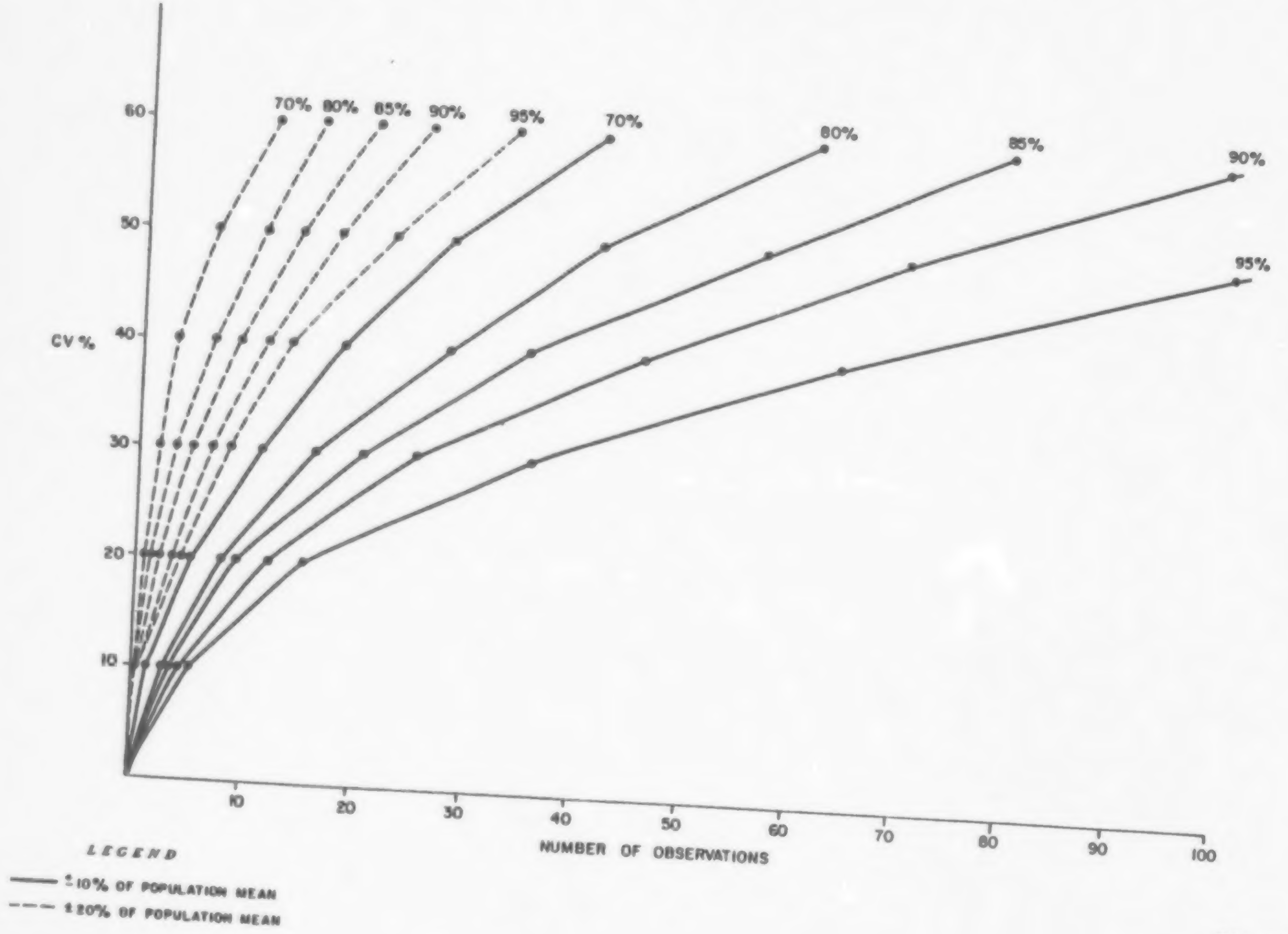

RELATIONSHIP BETWEEN VARIABILITY
AND SAMPLING DENSITY

Figure 2. Adapted from Wilding 1972

4. SOIL SAMPLING PROCEDURES

Soil sampling can be purposive or random. The former consists of sampling typical or average occurrences to confirm a soil scientist's hypothesis of what soil is expected on a given landscape unit (Miller et al. 1980). While purposive sampling is the rule rather than the exception, there are many objections to this sampling procedure:

1. The results rely heavily on the personal judgement of the surveyor;
2. There is no way to verify, except by checking random transects in the field (Arnold 1979), the quality of the surveyor's judgement;
3. There is no way of communicating the expert's confidence in his choice - no estimates of error are possible and objective conclusions cannot be drawn about the soil population (Mapping Systems Working Group 1981);
4. The survey can be biased in that sampling preference is given to one part of the population (Webster 1979).

Random sampling is probability sampling and benefits from the advantages accruing to the use of probability theory (McCammon 1975). Random sampling does not mean "casual" or "haphazard"; paradoxically, random sampling is achieved in practice only by following strict rules. This means that there must be ways of identifying the individual in a population and of selecting the individuals without bias.

Random sampling procedures are termed simple, stratified or systematic, depending on how the sampling points are selected. A simple random sample is a sample obtained such that each possible combination of sample units (n) has an equal chance of being selected (Petersen and Calvin 1965). Although random sampling is the best way to ensure both an unbiased estimate of the mean and an unbiased estimate of significance and confidence limits (Cline 1944), uneven coverage of an area often means that simple random sampling is inefficient in describing an area.

In stratified random sampling, the total area is broken into a number of cells or subpopulations and a simple random sample is taken from each cell. This method is used to make statements about each cell or subpopulation separately, and to increase the precision of estimates ove the entire area (Petersen and Calvin 1965, Webster 1979). In order for stratified random sampling to be more precise than a simple random method, the stratification must eliminate some variation attributable to sampling error. Stratification must make the sampling units (cells) more homogeneous than the population as a whole. The basis of effective stratification may be another variable related to the property of interest (covariance), previous knowledge about the distribution of the variability (multistage sampling or pre-analysis of variability data) or a simple reduction in geographical distance (the smaller the area, the less the soil variability). The basis for stratification and the compromises associated with choosing one method over another are discussed briefly in Section 6, Soil Classification.

The gain in efficiency of stratified over simple random sampling is due primarily to better coverage of an area. Systematic sampling, a scheme in which selected units are at regular distances from each other, is a further attempt in guaranteeing improved coverage. Sampling points can be located at regular intervals on a grid as shown in Figure 3 or unaligned with a constant interval in rows and columns as in Figure 4.

In addition to a gain in precision (Finney 1948, Williams 1956), systematic sampling is preferred for mapping procedures. The production of high quality maps requires complete and even coverage, unbiased sampling and the most relative precision possible when sample numbers and costs have been fixed.

Figure 5 is an example of a computer-interpolated map of topsoil depths produced from a systematic sampling program. Environmental scientists and managers interested in sulphur impact might want the sample point to represent sulphur deposition rates or soil pH status; the principles remain the same - soil properties can be systematically sampled and mapped so that interpolated isopleths are used to represent environmental gradients.

There are two commom criticisms levelled against systematic sampling: (1) a loss in precision in comparison to simple random or stratified random methods when the population has a periodic trend in variation which corresponds to the sampling interval; and (2) the

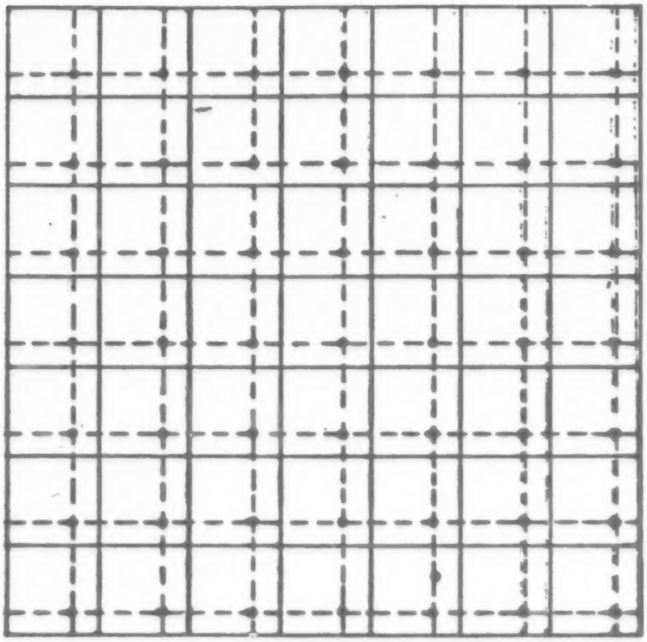

Figure 3. A systematic sample of 49 points (Webster 1979).

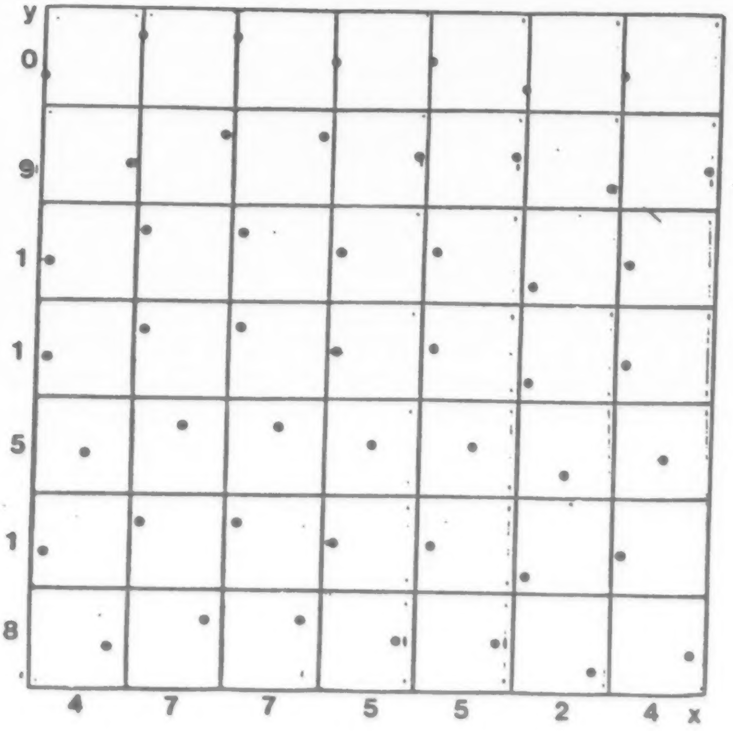
y
0
9
1
1
5
1
8
4
7
7
5
5
2
4
x

Figure 4. An unaligned sample (Webster 1979).

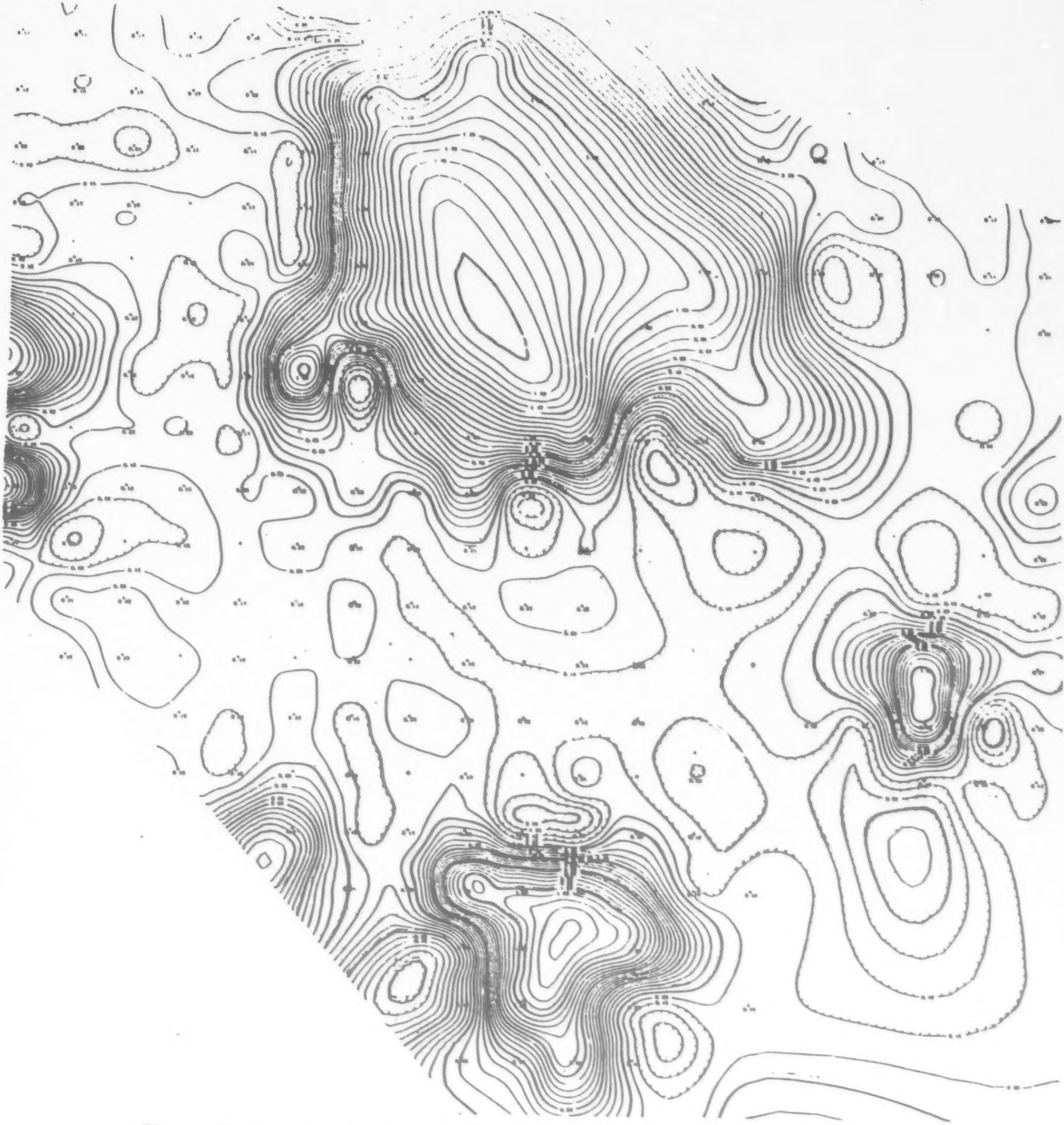

Figure 5. A computer-interpolated map of topsoil depths with isopleths at 5 cm intervals.

difficulty in estimating sampling error from the sample itself. In response to the first criticism it is recommend that a grid pattern be chosen that is unrelated in spacing and orientation and that sample numbers be increased (Webster 1979). Petersen and Calvin (1965) show several methods for estimating sampling error from systematic samples and point out what assumptions are made for each.

5. NESTED SAMPLING

Nested or hierarchial sampling is a more sophisticated approach to a quantitative analysis of soil variability. The objective of this procedure is to partition the variability of any soil property (or group of soil properties) according to changes in parent material (Nortcliff 1976), physiography (Molletor et al. 1980) or a spatial proximity (Youden and Mehlich 1937). On the basis of this analysis, it is then possible to design the most efficient sampling scheme to derive acceptable confidence and prediction limits for critical environmental variables.

Nested sampling design, in soil studies, divides the total area into classes, which are in turn divided into smaller classes, and so on. The result can be portrayed as a hierarchy or tree. Figure 6 shows the nested sampling design used by Youden and Mehlich (1937) and diagrammed by Webster (1979). An analysis of variance of the different components of pH in the Youden and Mehlich (1937) study are represented in Table 2.

By calculating the components of variability, a cost effective, efficient sampling program can be designed. In general, sampling should be increased at those stages where the component contribution to variance is highest. Webster (1979) used this specific example to show that total sample size could be reduced to 25% of the original and still the precision of predicting mean pH would be improved.

6. SOIL CLASSIFICATION

Soil mapping attempts to break the continuum of soil types on a landscape into a limited number of units on the basis of properties relevant to the survey objectives (Mapping Systems Working Group 1981).

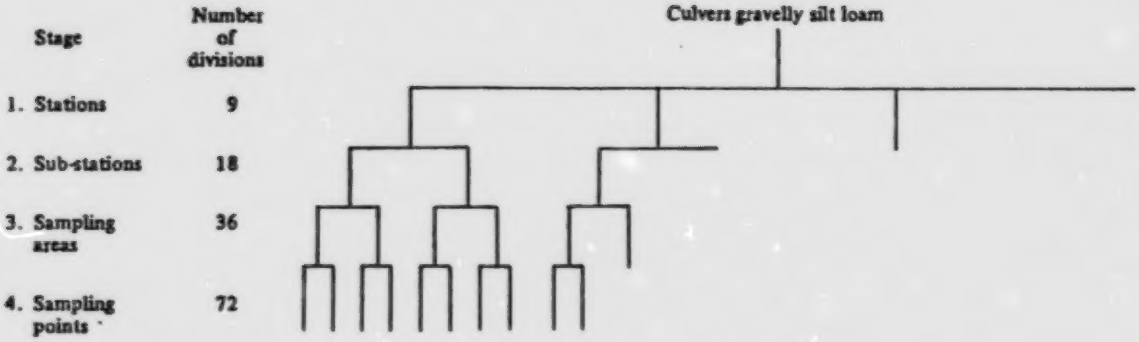
Stage
Number of divisions
Culvers gravelly silt loam
1. Stations
9
2. Sub-stations
18
3. Sampling areas
36
4. Sampling points
72

Figure 6. A nested sampling scheme for determining the pH of the culvers gravelly silty loam (Webster 1979).

Table 2. Components of variance of pH in a Culvers gravelly silt loam (adapted from Youden and Mehlich, and Webster 1977).

Source	Distance	Variance in pH	% Total Variance
Between stations	1600 m	0.0282	39.7
Between sub-stations within stations	305 m	0.0234	32.9
Between areas within sub-stations	30.5 m	0.0055	7.8
Between points within areas (residual)	3.0 m	0.0139	19.6

Soil classification schemes which take account of many properties of the soil or divide the population at natural discontinuities are said to be "natural". These types of survey and mapping procedures are also called general-purpose classifications (Webster 1979). The objective of all general-purpose soil surveys is to delineate the landscape into soil units that contain less variable soil conditions than the total population of soils (Miller et al. 1980). In this sense general-purpose classification and mapping systems are the published results of a hypothesis regarding the association of soil and landscape and are also methods of stratification.

The use of general-purpose soil survey reports and maps can be misleading to an environmental scientist when the basis of sampling and the delineation of soil boundaries is not understood. Information is often collected with an intentional bias - to confirm or reject the soil surveyor's hypothesis of what soil is expected on a given landscape unit - and not to support conclusions about the range of individual properties within a mapping or taxonomic unit.

The environmental scientist, however, wants to know about certain properties; the mean value, the distribution and the confidence limits that can be placed on them. Almost without exception the general-purpose soil maps produced by soil survey throughout the world do not contain reliable information about the location and dispersion of values for any soil property. This information must be gathered subsequent to the survey.

Dissection is a different approach to soil survey and classification and is discussed in detail by Webster (1979). Classes of soil are created by dividing the range of variation of a simple soil property at fixed points. Dissection is used when values can be chosen for technological need, as in "critical" levels of available phosphorus for agricultural purposes (Nelson and Anderson 1977), or to achieve a predetermined number of classes. Divisions are to be "useful", not "natural" (Webster 1979).

As a more pertinent environmental example, dissection can be applied to the classification of soils acidified as a result of sulphur deposition. In those cases where amelioration is necessary and is to be based on soil pH levels and buffering capacity (Baker and Chae

1977), dissection by reason of lime requirement is simple, straightforward and cost effective.

If the management of the soil depends on several properties, the classes are created by dividing the corresponding property ranges at critical levels. When the number of properties and divisions are so numerous that they become unmanageable, more sophisticated numerical techniques, such as principle component analysis (Holland 1969) or multiple discriminate analysis (Webster and Burrough 1974) can be used.

7. SAMPLING VERSUS CLASSIFICATION

The purpose of soil classification and mapping is to create soil classes which have less variability in the properties of interest than that contained in the original population. It is from this basis that prediction can be made more exact and generalization more useful. If classification does not reduce the variability or if it costs more to classify than to sample, then it is better to measure the properties (sample) in the field.

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A DECADE OF OBSERVING SOIL pH IN THE VICINITY OF THE SHELL CANADA RESOURCES LIMITED WATERTON GAS PLANT

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J.A. LORE[1], E.A. MCCULLOCH[1]

ABSTRACT

No trend in pH change has been observed in natural soil profiles over ten years in the vicinity of the Shell Waterton Gas Plant. This does not support the observations of Laverty and Carson on soil profiles around two Alberta gas plants. The results do not support predictions of possible pH change made from short-term exposure of potted soils to gas plant emissions.

[1] McKinnon, Allen & Associates (Western) Ltd., Calgary, Alberta

1. INTRODUCTION

Sulphur and its compounds can result in soil acidification. A decline in pH of soil in pots has been demonstrated to be related to SO_2 emissions. (Nyborg et al 1975; McKinnon & Allen 1976). Terraglio and Marganelli (1966) showed that SO_2 in the atmosphere is absorbed by all soils. Soils accumulate SO_2 from a polluted atmosphere by rainfall, adsorption and particulate fallout (Nyborg et al. 1975). Katz (1949) found acid soils in the vicinity of SO_2 emission sources, and suggested this acidification occurred in low calcium soil. Laverty and Carson (1977) found pH changes in normal profiles downwind of SO_2 emission sources. The original soil pH was not known, so comparisons were made with other areas, not in the prevailing wind direction. It was concluded that acidification appeared to have occurred downwind from 2 to 4 miles to at least 12 miles.

Bowser and Leat (1958) and Elliot both showed that soil pH fluctuations of ± 1.0 units can occur normally within one season.

Wet bare potted soils and pots growing barley and alfalfa can gain sulphur in high emission areas (McKinnon & Allen 1976), (Hua Hsu and G.W. Hodgeson, 1977).

The Shell Waterton Gas Plant had been operating for about 10 years when this study was initiated in 1972. Soil pH was monitored to determine if a soil pH change was occurring. Soil buffer curves from 1973 and 1980 were compared.

2. MATERIALS AND METHODS

Six pairs of plot sites were established in 1972. One emission zone site was paired with one control zone site based on historical sulfation monitoring. The two sites in each pair were similar in topography and elevation. The six emission sites were labelled Riviere, McRae, Robertson, Bruder, Bonertz and Jack, with Riviere being at the point of highest SO_2 concentration. The six control sites were Carlson, Cridland, Lynch-Staunton, Opperman, McNab and Dick, with Lynch-Staunton having the lowest SO_2 concentration. Four sites were under cultivation, the rest in grass.

Composite samples of soil from each site were taken before cultivation in June, 1972, and again in the fall of 1972.

In the spring of 1973, the plots were seeded in three replicates with a split plot design. The crops seeded were alfalfa, barley, brome and brome/alfalfa mixture. Each had a fertilizer subtreatment. Six of the pairs were naturally acidic, i.e., below pH 6.0. At these sites an extra alfalfa treatment was included in each replicate and was limed, as was the brome/alfalfa mixture treatment. Soil samples were taken from barley nil plots at the 0-15 cm depth in the fall of 1973.

The barley nil plots were sampled at the 0-15 cm and 15-30 cm depths, both in the spring and fall, from 1974 to 1981. The alfalfa nil plots were sampled at the 0-15 cm depth from 1976 to 1981, both in the spring and fall. Ten to twelve probes were taken to form a composite sample for each replicate.

Samples were air-dried and ground through a 2 mm mesh screen. A 1 to 2.5 soil to water mixture was stirred at 10 minute intervals for 30 minutes and then let stand for 1 hour. A pH reading on each sample was taken.

Some difficulties in locating plots were experienced at the Bruder, Cridland, and Dyck sites in 1980 and the spring of 1981, resulting in gaps in the data for these sites.

Buffer curves for selected plot samples were determined for 1973 and 1980.

The pH of the barley nil 0-15 cm and 15-30 cm depths was compared. The pH values of the 0-15 cm depths of all the sites were compared with the Lynch-Staunton (best control) site. The data were compared between pairs. A linear regression was run to ascertain the slope of pH plotted against time.

After 1976, the various treatments were stopped and the plots were farmed by the original owners again. At this time, sampling of the Bonertz and McNab plots was halted. The locations of the remaining 10 sites were established by survey and permanent markers installed. Most of the plots are now in pasture.

3. RESULTS AND DISCUSSION

Figure 1 (see Appendix 1) shows the location of the sites relative to the SO_2 emission source. Shell Waterton emitted approximately 91 tonnes of S per day until 1976. Tail gas clean up reduced this to about 36 tonnes per day after 1976. The Gulf Plant was emitting approximately 5 to 6 tonnes per day. Prevailing winds are from the southwest.

Tables 1, 2 and 3 (see Appendix 2)report the average pH of three replicates at each site, for the depths and plots sampled. Yearly or even seasonal changes are obvious and occasionally are of the order reported by Bowser and Leats (1958) and Elliot. Figures 2, 3 and 4 depict the information graphically. There is agreement between the sites regarding the annual and/or seasonal change.

The data indicate that long term projections based on measurements over a short term can be misleading, due in part to annual and seasonal pH fluctuations. For example, the trend from 1972 to 1974 was consistent in all the data, and if projected, would have indicated a serious pH drop. Without data from a suitable number of control sites, the pH drop at the emission sites would have suggested an erroneous conclusion.

Consistent pH differences were found between replicates at some sites. The plots were 6.1 M x 1.8 M for naturally acidic sites and 6.1 M x 2.3 M for non-acidic sites. Table 4 (see Appendix 2) compares replicate data for 2 sites, which shows the agreement among replicates. The Riviere site had very close agreement among replicates, while the Opperman site had the least agreement among replicates.

It is apparent from the data in Table 4 that samples must be from the exact location, year after year, to yield meaningful results.

Linear regressions were calculated for each replicate of the barley nil, 0-15 cm depths. The slopes were essentially zero over the 9-year time frame, and no correlation was found between pH and time.

Any acidifying effect of SO_2 may be illustrated by comparing the pH of the 0-15 cm depths to the 15-30 cm depths. It would be expected that the 0-15 cm depths would acidify first. Figures 5 to 9 (see Appendix 1) show these data in graphic form. The emission sites consistently have a larger pH difference between the two depths. A linear regression was calculated on this difference for 4 sites, and is shown in Table 5. The slopes are very close to zero, and at both emission sites are negative.

A similar soil pH comparison was made between the barley nil 0-15 cm depths at Riviere (the highest SO_2 site) and Lynch-Staunton (the lowest SO_2 site). The slope was essentially zero ($M = .006$) and there was no correlation ($r = .177$).

Buffer curves were established for most of the sites. Figures 10 and 12 show the curves in 1973, and Figures 11 and 13 show the curves in 1980 for Replicate 2 at Riviere and Lynch-Staunton. The curves have a characteristic shape for each site. The Riviere site soil has less buffering capacity (more subject to acidification) than the Lynch-Staunton site soil. The addition of .2 milliequevalents of acid to ten grams of soil results in a pH drop of .6 to .7 at Riviere and only .1 at Lynch-Staunton. It would be expected that the difference in soil pH between the Riviere site and the Lynch-Staunton site would increase over time if acidification was occurring due to SO_2 emissions. None of the data support this hypothesis. Therefore, it is concluded that SO_2 emissions from the Shell Waterton Gas Plant have not acidified soil in the emission zone over 10 years of observation.

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APPENDIX 1: FIGURES

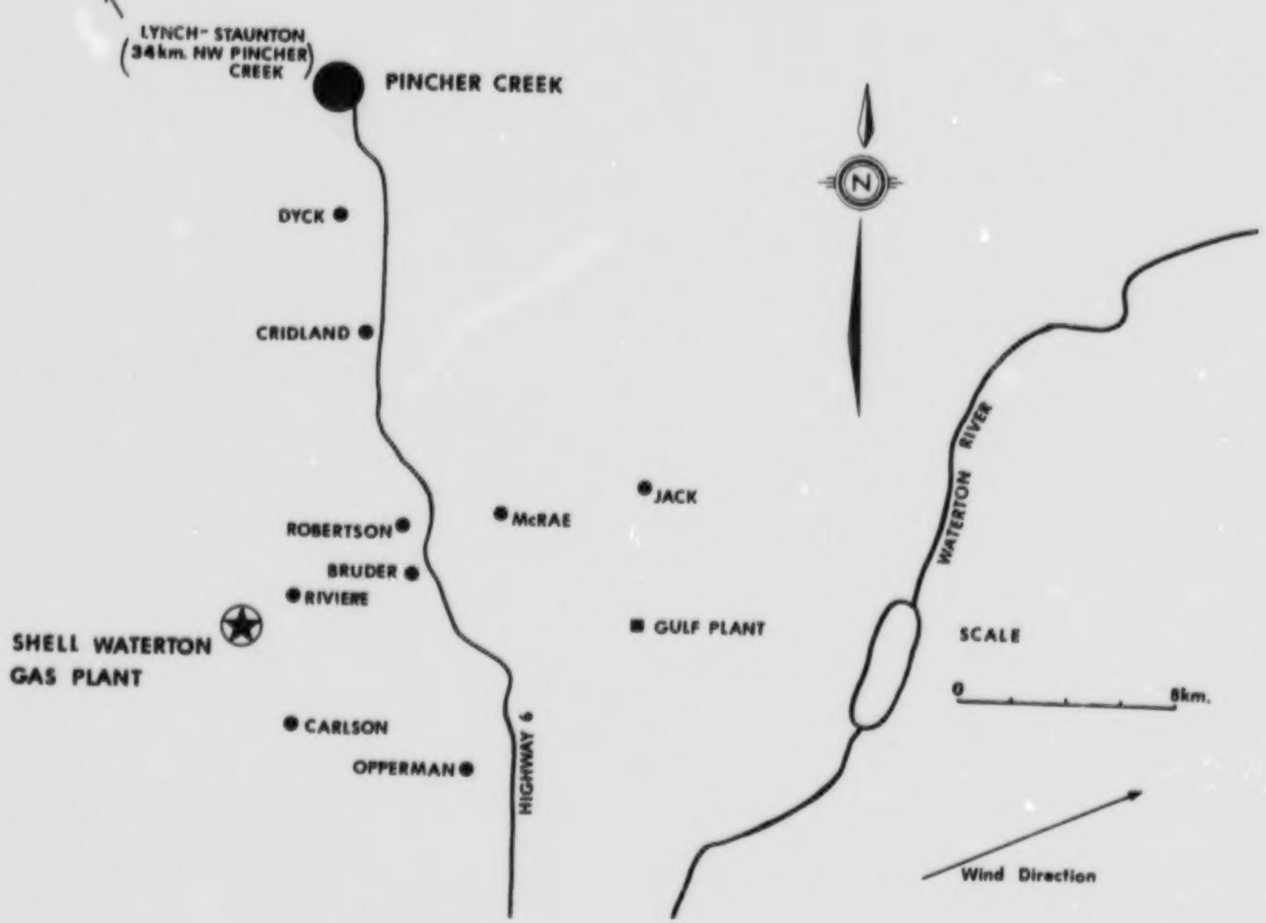

LYNCH- STAUNTON
(34km. NW PINCHER CREEK)
PINCHER CREEK
N
DYCK
CRIDLAND
ROBERTSON
McRAE
JACK
BRUDER
RIVIERE
SHELL WATERTON GAS PLANT
GULF PLANT
CARLSON
OPPERMAN
HIGHWAY 6
WATERTON RIVER
SCALE
0
8km.
Wind Direction

Figure 1. Location of Soil Sampling Sites and Gas Plants

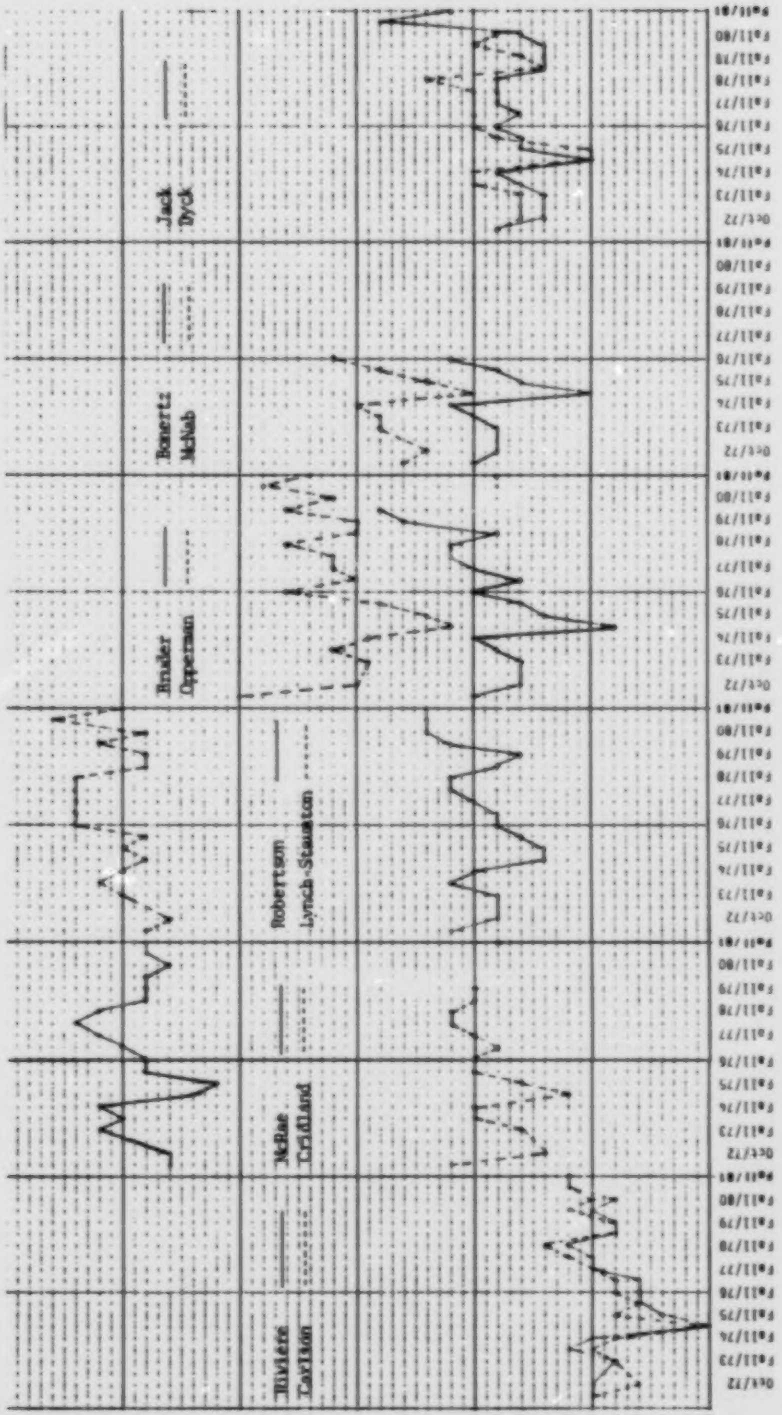


Figure 2. Waterton Plant Agricultural Environmental Program
Average Barley Nil Soil pH 0-15 cm Depth

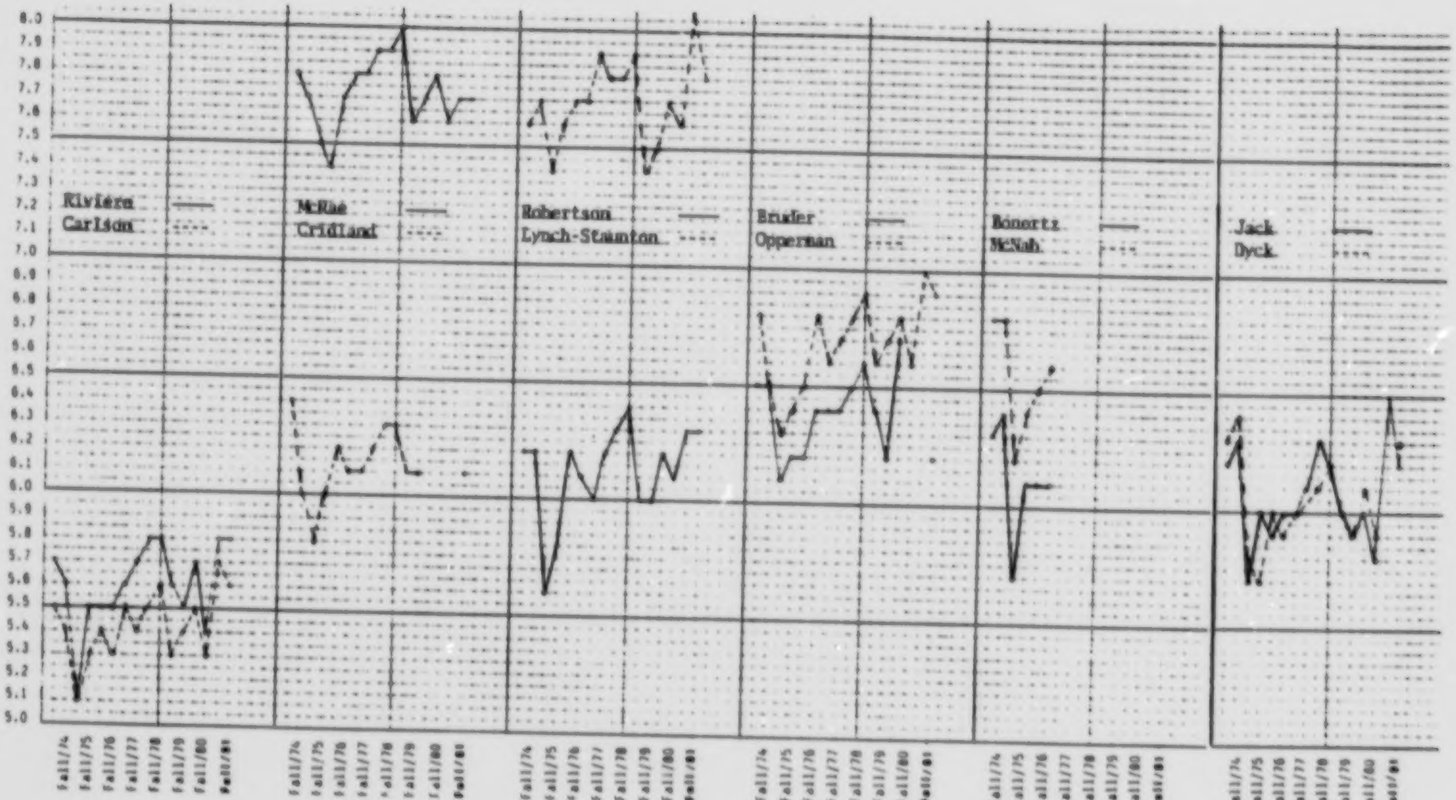


Figure 3. Waterton Plant Agricultural Environmental Program Average Barley Nil Soil pH 15-30 cm Depth

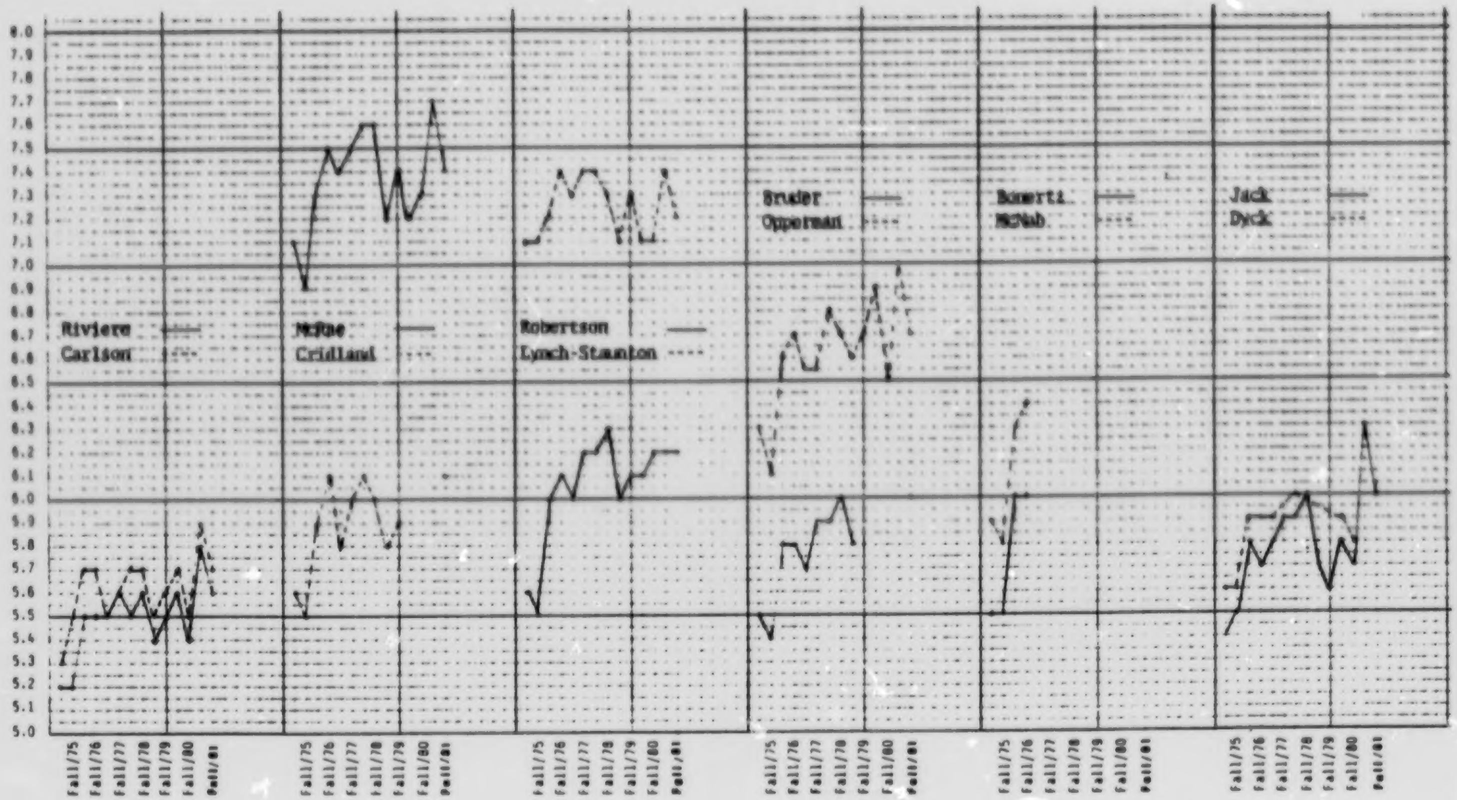


Figure 4. Waterton Plant Agricultural Environmental Program Average Alfalfa Nil Soil pH 0-15 cm Depth

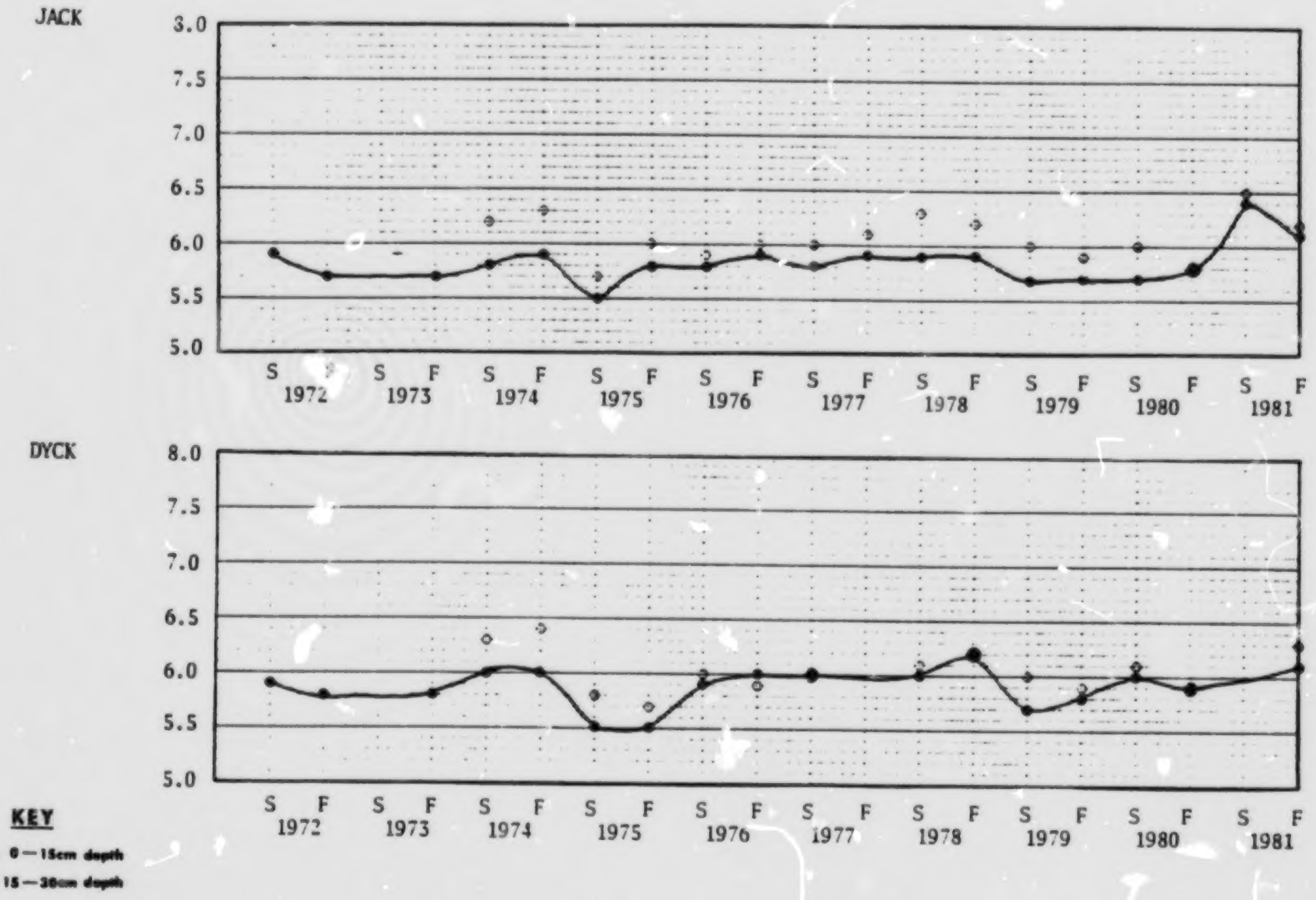


Figure 5. Waterton Plant Agricultural Environmental Program
Average Barley Nil Soil pH: 1972 - 1981

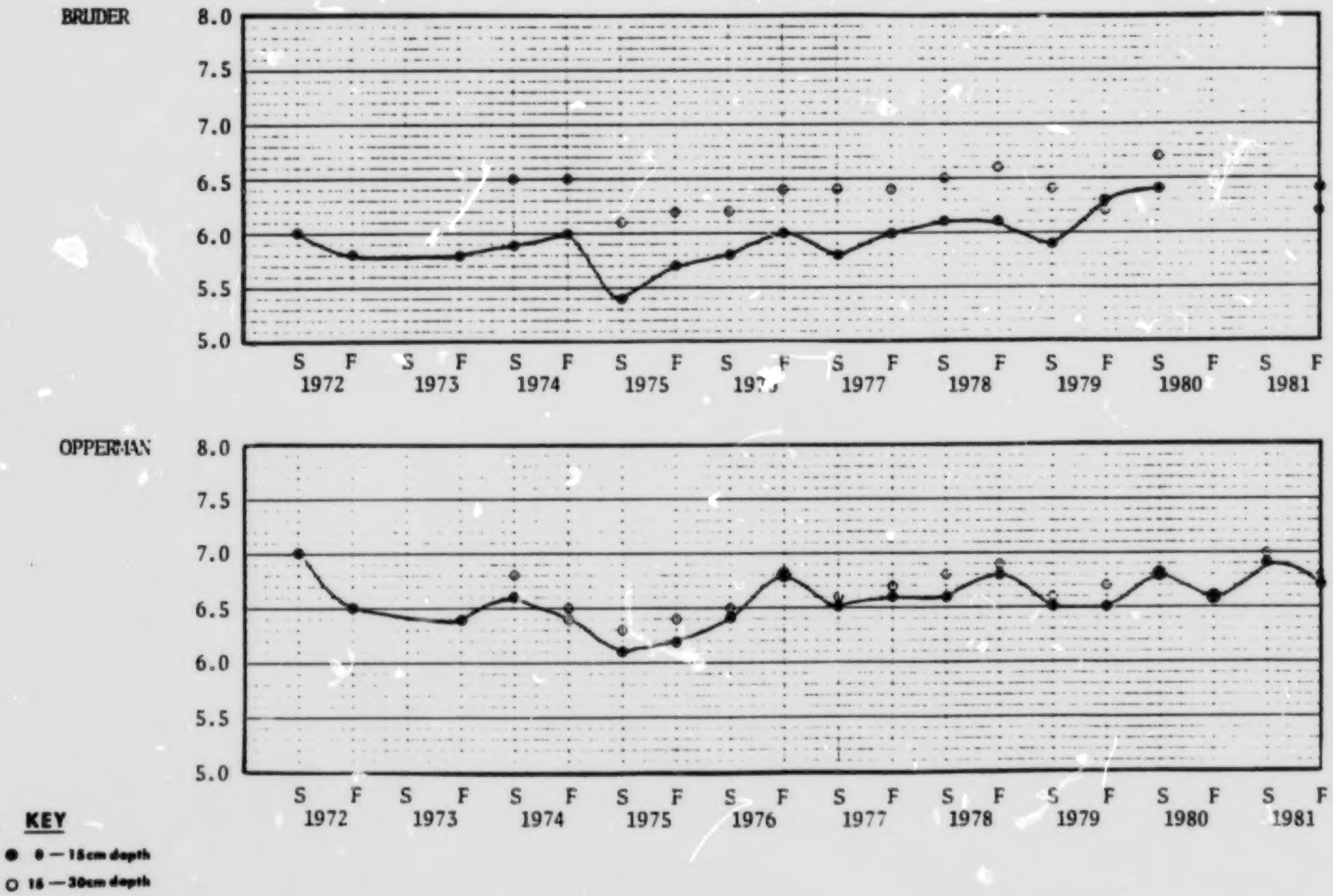


Figure 6. Waterton Plant Agricultural Environmental Program
Average Barley Nil Soil pH: 1972 - 1981

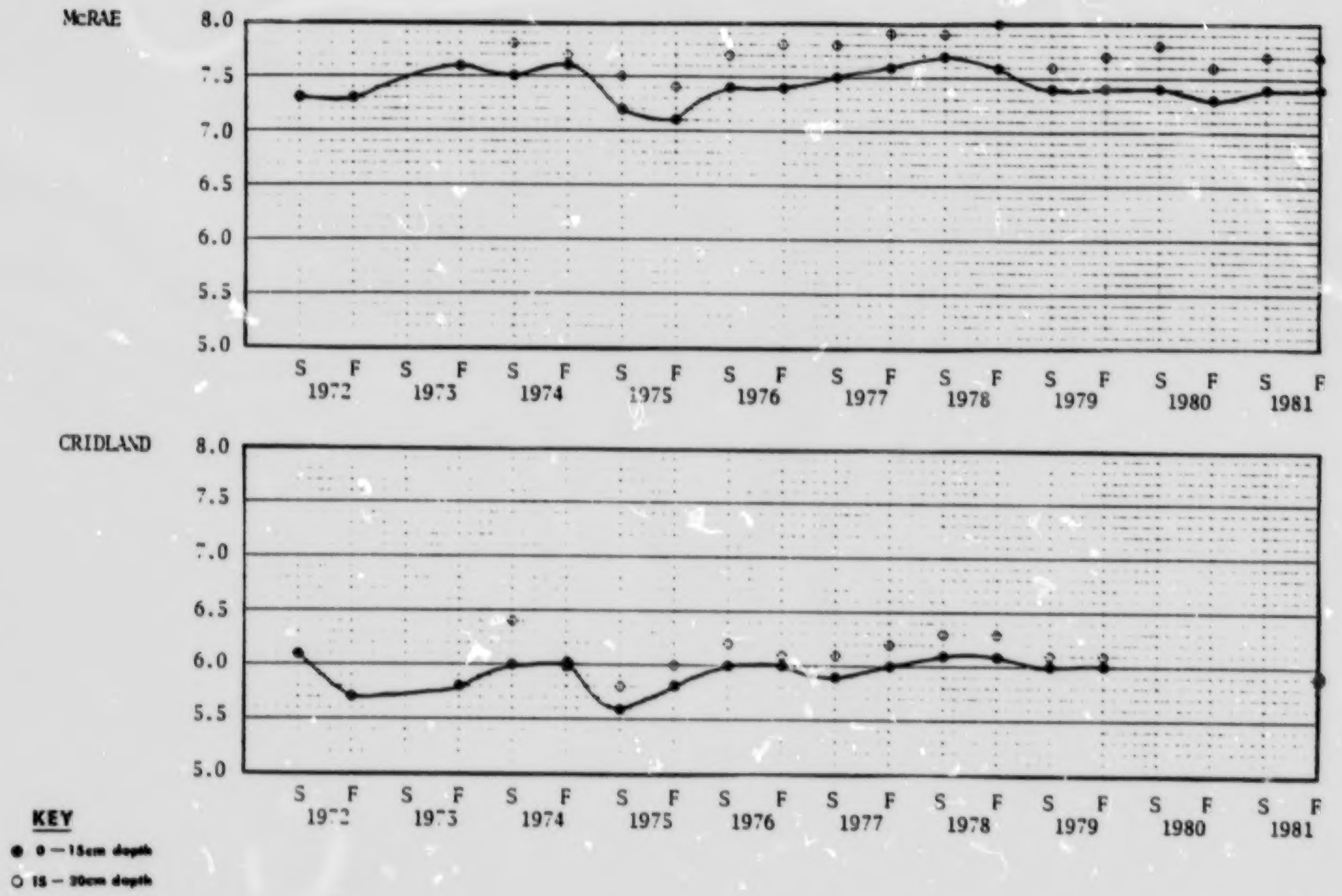


Figure 7. Waterton Plant Agricultural Environmental Program
Average Barley Nil Soil pH: 1972 - 1981

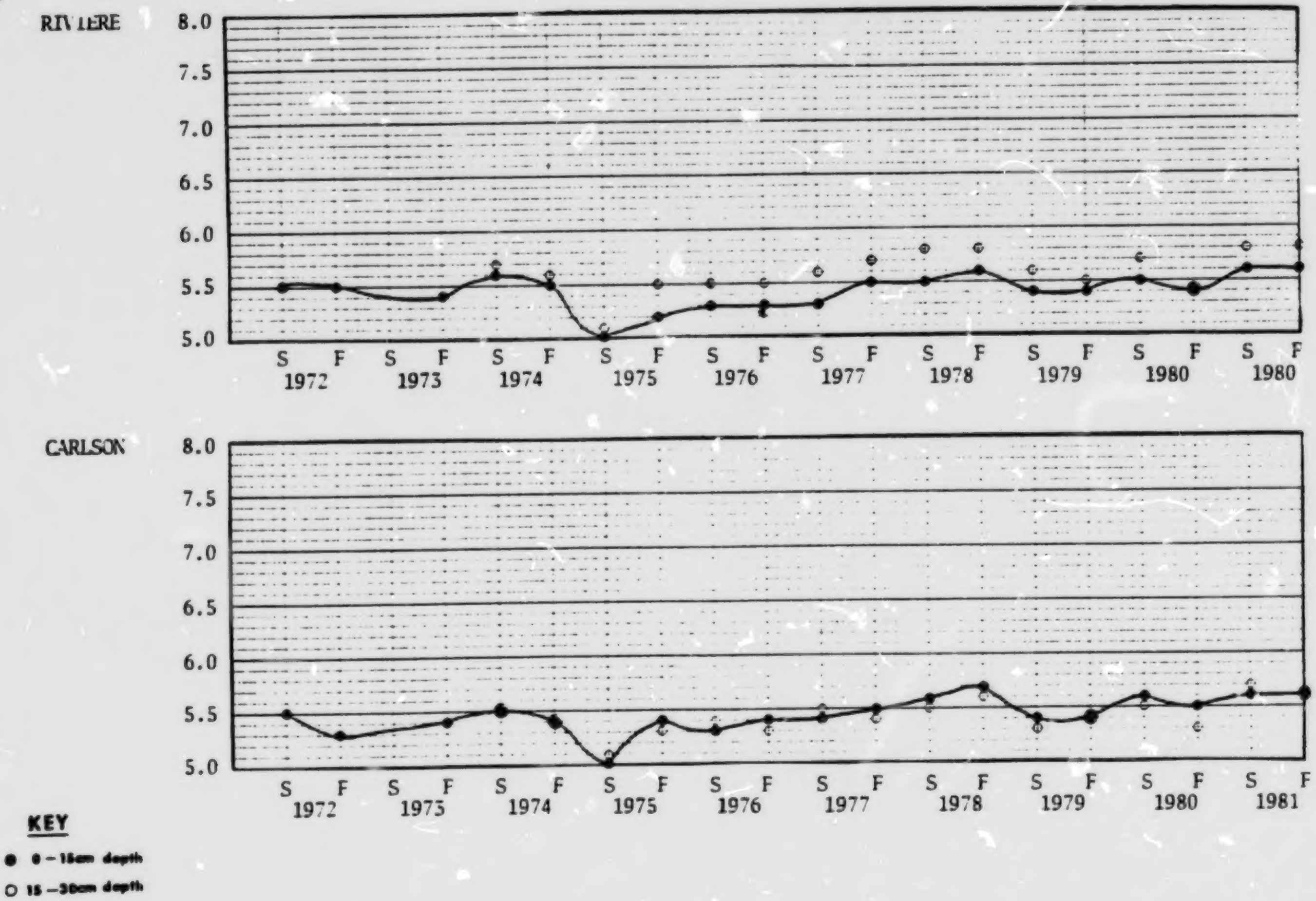


Figure 8. Waterton Plant Agricultural Environmental Program
Average Barley Nil Soil pH: 1972 - 1981

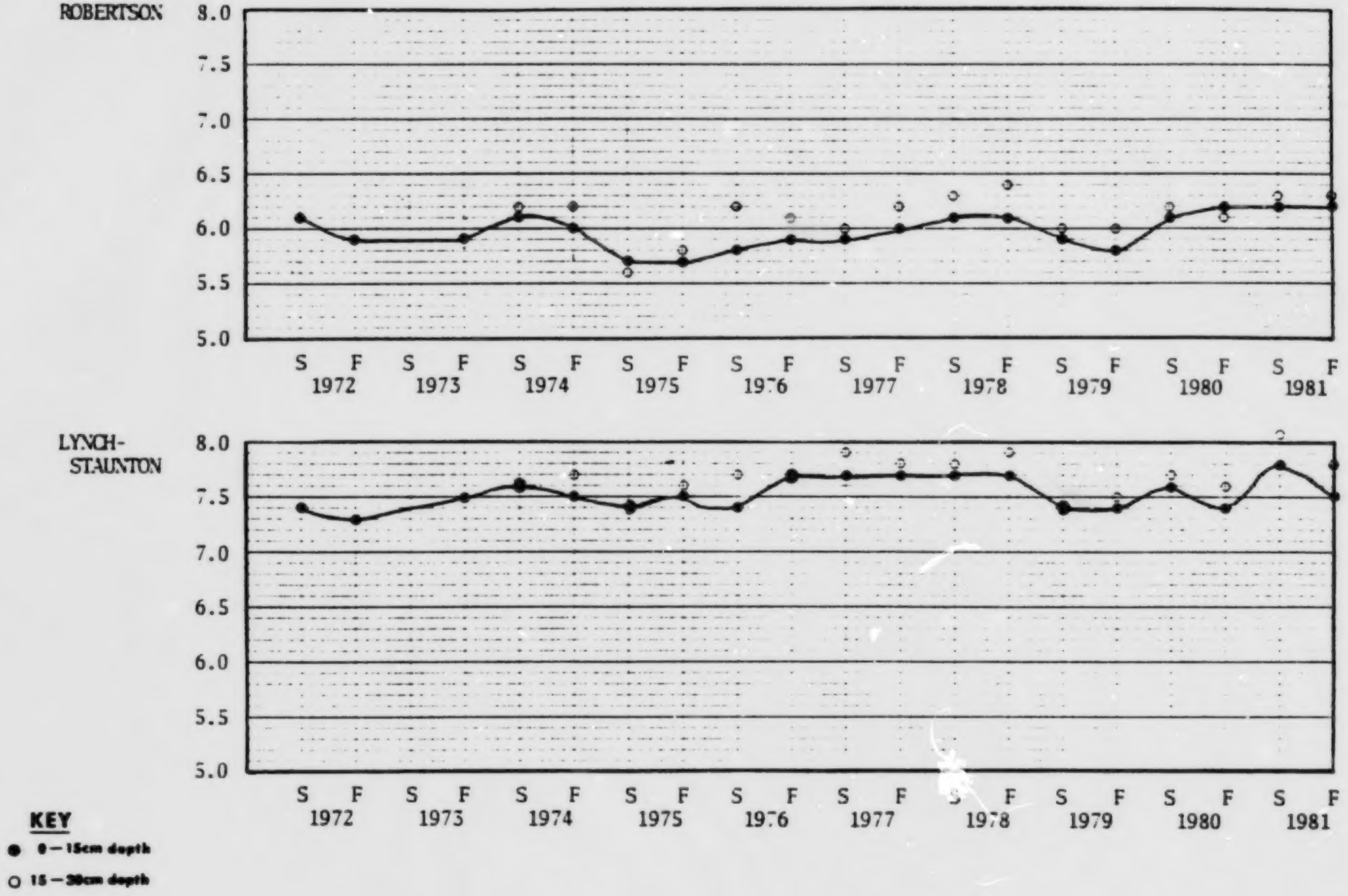
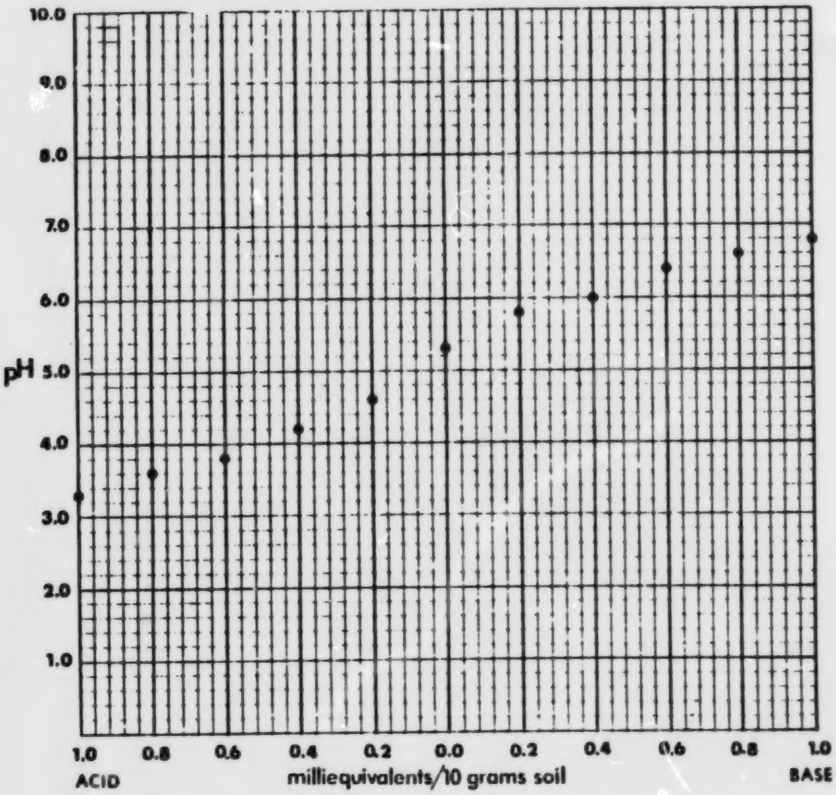


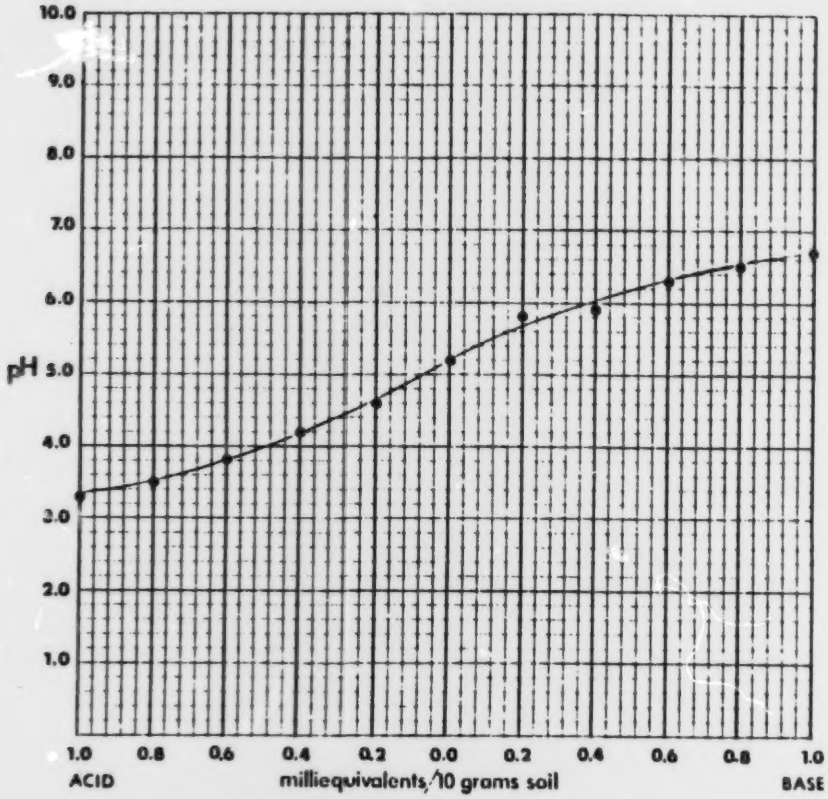
Figure 9. Waterton Plant Agricultural Environmental Program
Average Barley Nil Soil pH: 1972 - 1981



Milliequivalents Added (10 grams soil)		pH After 3 Days*
Acid	1.0	3.3
	0.8	3.6
	0.6	3.8
	0.4	4.2
	0.2	4.6
	0.0	5.3
Base	0.2	5.8
	0.4	6.0
	0.6	6.4
	0.8	6.6
	1.0	6.8

* 1:2.5 ratio of soil to liquid.

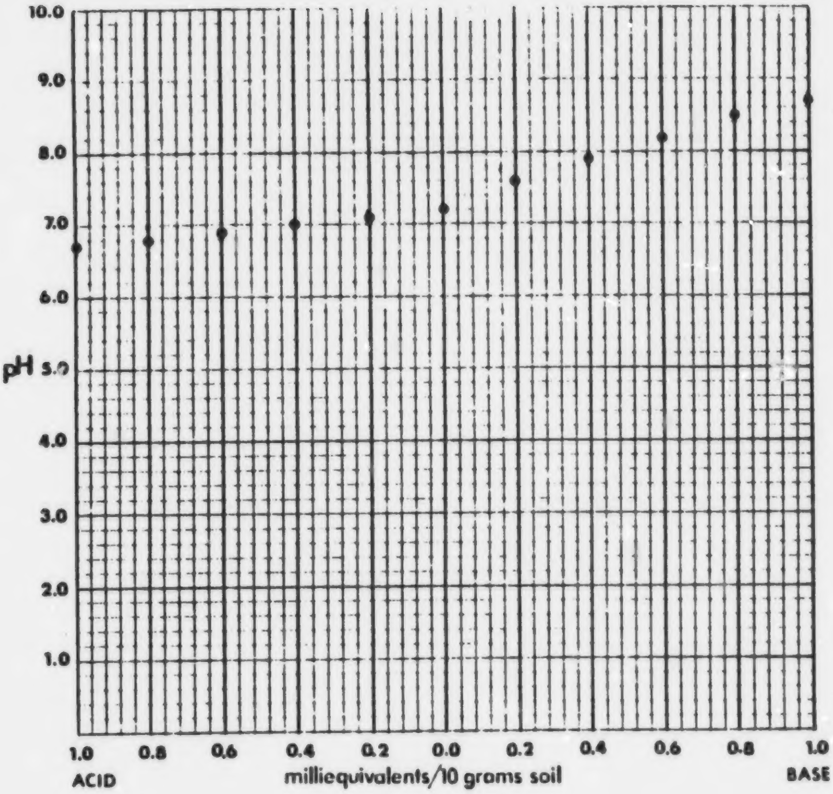
Figure 10. Soil Buffer Curve
Riviere: R2: Barley Nil 0-15 cm depth
Fall, 1973



Milliequivalents Added (10 grams soil)		pH After 3 Days*
Acid	1.0	3.3
	0.8	3.5
	0.6	3.8
	0.4	4.2
	0.2	4.6
	0.0	5.2
Base	0.2	5.8
	0.4	5.9
	0.6	6.3
	0.8	6.5
	1.0	6.7

* 1:2.5 ratio of soil to liquid.

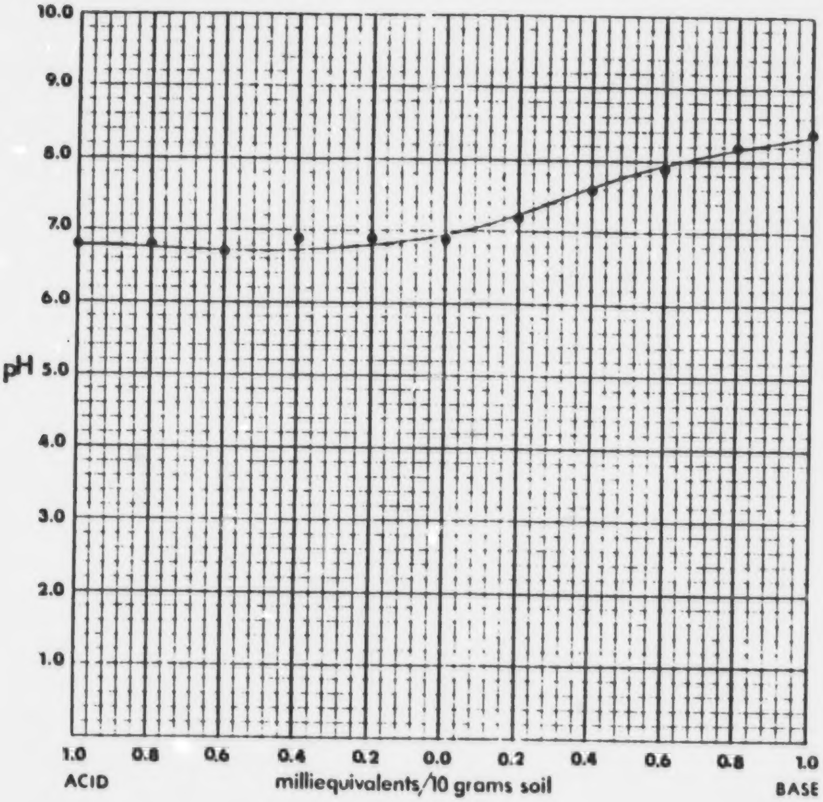
Figure 11. Soil Buffer Curve
Riviere: R2: Barley Nil 0-15 cm depth
Fall, 1980



Milliequivalents Added (10 grams soil)		pH After 3 Days*
Acid	1.0	6.7
	0.8	6.8
	0.6	6.9
	0.4	7.0
	0.2	7.1
	0.0	7.2
Base	0.2	7.6
	0.4	7.9
	0.6	8.2
	0.8	8.5
	1.0	8.7

* 1:2.5 ratio of soil to liquid.

Figure 12. Soil Buffer Curve
Lynch-Staunton: R2: Barley Nil 0-15 cm depth
Fall, 1973



Milliequivalents Added (10 grams soil)		pH After 3 Days*
Acid	1.0	6.8
	0.8	6.8
	0.6	6.7
	0.4	6.9
	0.2	6.9
	0.0	6.9
Base	0.2	7.2
	0.4	7.6
	0.6	7.9
	0.8	8.2
	1.0	8.4

* 1:2.5 ratio of soil to liquid.

Figure 13. Soil Buffer Curve
Lynch-Staunton: R2: Barley Nil 0-15 cm depth
Fall, 1980

APPENDIX 2: TABLES

Table 1. Waterton Plant Agricultural Environmental Program
Average* Barley Nil Soil pH 0-15 cm depth

Site	Zone	June 1972	Oct. 1972	Fall 1973	Spr. 1974	Fall 1974	Spr. 1975	Fall 1975	Spr. 1976	Fall 1976	Spr. 1977	Fall 1977	Spr. 1978	Fall 1978	Spr. 1979	Fall 1979	Spr. 1980	Fall 1980	Spr. 1981	Fall 1981
Riviere	E	5.5	5.5	5.4	5.6	5.5	5.0	5.2	5.3	5.3	5.3	5.5	5.5	5.6	5.4	5.4	5.5	5.4	5.6	5.6
Carlson	C	5.5	5.3	5.4	5.5	5.4	5.0	5.4	5.3	5.4	5.4	5.5	5.6	5.7	5.4	5.4	5.6	5.5	5.6	5.6
McRae	E	7.3	7.3	7.6	7.5	7.6	7.2	7.1	7.4	7.4	7.5	7.6	7.7	7.6	7.4	7.4	7.4	7.3	7.4	7.4
Cridland	C	6.1	5.7	5.8	6.0	6.0	5.6	5.8	6.0	6.0	5.9	6.0	6.1	6.1	6.0	6.0		‡	‡	5.9
Robertson	E	6.1	5.9	5.9	6.1	6.0	5.7	5.7	5.8	5.9	5.9	6.0	6.1	6.1	5.9	5.8	6.1	6.2	6.2	6.2
Lynch-Staunton	C	7.4	7.3	7.5	7.6	7.5	7.4	7.5	7.4	7.7	7.7	7.7	7.7	7.7	7.4	7.4	7.6	7.4	7.8	7.5
Bruder	E	6.0	5.8	5.8	5.9	6.0	5.4	5.7	5.8	6.0	5.8	6.0	6.1	6.1	5.9	6.3	6.4	‡	‡	5.9
Opperman	C	7.0	6.5	6.4	6.6	6.4	6.1	6.2	6.4	6.8	6.5	6.6	6.6	6.8	6.5	6.5	6.8	6.6	6.9	6.7
Bonertz**	E	6.0	5.9	5.9	6.0	6.1	5.5	5.8	5.9	6.1										
McNab**	C	6.3	6.2	6.4	6.4	6.5	6.0	6.2	6.4	6.6										
Jack	E	5.9	5.7	5.7	5.8	5.9	5.5	5.8	5.8	5.9	5.8+	5.9	5.9	5.9	5.7	5.7	5.7	5.8	6.4	6.1
Dyck	C	5.9	5.8	5.8	6.0	6.0	5.5	5.5	5.9	6.0	6.0	---	6.0	6.2	5.7	5.8	6.0	5.9	‡	6.1

* All 1972 soil samples were a composite sample from the whole plot. The plots were summerfallowed during 1972. From 1973 to 1981, the pH values are the average for three replicates.

** The Bonertz and McNab sites were not sampled following 1976.

+ Plot was too wet for complete sampling, one replicate only.

‡ No sample taken.

Table 2. Waterton Plant Agricultural Environmental Program
Average* Barley Nil Soil pH 15-30 cm depth

	Zone	Spring 1974	Fall 1974	Spring 1975	Fall 1975	Spring 1976	Fall 1976	Spring 1977	Fall 1977	Spring 1978	Fall 1978	Spring 1979	Fall 1979	Spring 1980	Fall 1980	Spring 1981	Fall 1981
Riviere	E	5.7	5.6	5.1	5.5	5.5	5.5	5.6	5.7	5.8	5.8	5.6	5.5	5.7	5.4	5.8	5.8
Carlson	C	5.5	5.4	5.1	5.3	5.4	5.3	5.5	5.4	5.5	5.6	5.3	5.4	5.5	5.3	5.7	5.6
McRae	E	7.8	7.7	7.5	7.4	7.7	7.8	7.8	7.9	7.9	8.0	7.6	7.7	7.8	7.6	7.7	7.7
Cridland	C	6.4	6.0	5.8	6.0	6.2	6.1	6.1	6.2	6.3	6.3	6.1	6.1	‡	‡	‡	5.9
Robertson	E	6.2	6.2	5.6	5.8	6.2	6.1	6.0	6.2	6.3	6.4	6.0	6.0	6.2	6.1	6.3	6.3
Lynch-Staunton	C	7.6	7.7	7.4	7.6	7.7	7.7	7.9	7.8	7.8	7.9	7.4	7.5	7.7	7.6	8.1	7.8
Bruder	E	6.5	6.5	6.1	6.2	6.2	6.4	6.4	6.4	6.5	6.6	6.4	6.2	6.7	‡	‡	6.2
Opperman	C	6.8	6.5	6.3	6.4	6.5	6.8	6.6	6.7	6.8	6.9	6.6	6.7	6.8	6.6	7.0	6.8
Bonertz**	E	6.3	6.4	5.7	6.1	6.1	6.1										
McNab**	C	6.8	6.8	6.2	6.4	6.5	6.6										
Jack	E	6.2	6.3	5.7	6.0	5.9	6.0	6.0+	6.1	6.3	6.2	6.0	5.9	6.0	5.8	6.5	6.2
Dyck	C	6.3	6.4	5.8	5.7	6.0	5.9	6.0	‡	6.1	6.2+	6.0+	5.9+	6.1	5.9	‡	6.3

* The pH values are the average from three replicates.

** The Bonertz and McNab sites were not sampled following 1976.

+ Only one replicate was sampled.

‡ No sample taken.

Table 3. Waterton Plant Agricultural Environmental Program
Average* Alfalfa Nil Soil pH 0-15 cm depth

Site	Zone	Spring 1975	Fall 1975	Spring 1976	Fall 1976	Spring 1977	Fall 1977	Spring 1978	Fall 1978	Spring 1979	Fall 1979	Spring 1980	Fall 1980	Spring 1981	Fall 1981
Riviere	E	5.2	5.2	5.5	5.5	5.5	5.6	5.5	5.6	5.4	5.5	5.6	5.4	5.8	5.6
Carlson	C	5.3	5.5	5.7	5.7	5.5	5.6	5.7	5.7	5.5	5.6	5.7	5.5	5.9	5.7
McRae	E	7.1	6.9	7.3	7.5	7.4	7.5	7.6	7.6	7.2	7.4	7.2	7.3	7.7	7.4
Cridland	C	5.6	5.5	5.9	6.1	5.8	6.0	6.1	6.0	5.8	5.9	+	+	+	6.1
Robertson	E	5.6	5.5	6.0	6.1	6.0	6.2	6.2	6.3	6.0	6.1	6.1	6.2	6.2	6.2
Lynch-Staunton	C	7.1	7.1	7.2	7.4	7.3	7.4	7.4	7.3	7.1	7.3	7.1	7.1	7.4	7.2
Bruder	E	5.5	5.4	5.8	5.8	5.7	5.9	5.9	6.0	5.8	+	+	+	+	6.0
Opperman	C	6.3	6.1	6.6	6.7	6.6	6.6	6.8	6.7	6.6	6.7	6.9	6.5	7.0	6.7
Bonertz**	E	5.5	5.5	6.0	6.0										
McNab**	C	5.9	5.8	6.3	6.4										
Jack	E	5.4	5.5	5.8	5.7	5.8	5.9	5.9	6.0	5.7	5.6	5.8	5.7	6.3	6.0
Dyck	C	5.6	5.6	5.9	5.9	5.9	+	6.0	+	+	+	5.9	5.8	+	6.0

* The pH values are the average from three replicates.
** The Bonertz and McNab sites were not sampled following 1976.
+ No sample taken.

Table 4. Waterton Plant Agricultural Environmental Program
Barley Nil, Soil pH 0-15 cm depth: Selected Sites

Riviere	R1	R2	R3
1974 Spring	5.59	5.49	5.58
1974 Fall	5.56	5.44	5.47
1975 Spring	5.00	5.00	5.30
1975 Fall	5.16	5.10	5.20
Opperman	**R1**	**R2**	**R3**
1974 Spring	7.02	6.49	6.34
1974 Fall	6.77	6.41	6.11
1975 Spring	6.40	6.00	5.88
1975 Fall	6.57	6.10	5.80

Table 5. Waterton Plant Agricultural Environmental Program Linear Regression of Barley Nil Soil pH Differences Between 0-15 cm and 15-30 cm depths: Selected Sites

	Slope M	Y Intercept	r
Riviere (emission)	-.0015	.19	.072
Carlson (control)	-.0127	.0527	.568
Lynch-Staunton (control)	+.0031	.0912	.135
Jack (emission)	-.0081	.296	.28

THE REACTION OF SO_2 EMISSIONS WITH SOILS

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R.W. PARKER[3]

ABSTRACT

A sample of a plow layer of a cultivated soil was set out in replicated containers 12 cm deep at 8 sites in the vicinity of 2 gas plants (up to 19 km downwind) and as well at 2 control sites. The containers were protected from rain but they were open to the air. After exposure from June to September the bare, moist soil at the 8 stations near the gas plants had gained on the average of 62 kg per ha of non-sulphate S, while there was little gain at the control sites. A substantial portion of the non-sulphate S in the containers moved vertically independently of the total N. These gains of S were smaller on another soil.

Subsequently, laboratory investigations have been undertaken on the rates of SO_2 sorption by soils and the effect on soils. Several preliminary results are unusual. Air-dried samples of two agricultural soils were treated at a rate of 400 µg S as SO_2 per g soil for only 15 minutes, and the soil pH was depressed by 1.7 and 1.4 units. This depression was not transitory. Treatment of the soils with 200 µg S as SO_2 per g soil decreased pH by approximately 1.0 units. Further, whether the soils were dry or moist, treated for 15 minutes, or treated in smaller doses over 40 days did not make a major difference to the effect on pH. Likewise, there was formation of non-soluble S regardless of those conditions.

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1. INTRODUCTION

1.1 SULPHUR DIOXIDE EMISSION

Sulphur dioxide is one of the major air pollutants discharged into the atmosphere by natural and industrial activities. Natural sources include volcanic activities, sea spray and aquatic and terrestial microbiological activities. Man-made sources include smelting and roasting of sulphur containing ores, the pulp and paper industry and processing of fossil fuels.

On a global scale about 150 x 10^6 metric tons of sulphur are being discharged annually by both natural and industrial activities (Kellog et al. 1972; Granat et al. 1975). About 60% of it is due to industrial activities (Husar and Husar 1978). Canada contributes about five % of the world's total sulphur emissions (Katz 1977).

In Alberta, annual industrial sulphur emissions amount to about 0.7 million metric tons (Sandhu 1978). Eighty-five percent of these are emitted to the atmosphere by oil sands and natural gas processing plants. It has been estimated that the Alberta oil sands contain some 980 billion barrels of crude bitumen in four deposit areas. The potential of the oil sands deposits is estimated to be 190 billion barrels of synthetic crude oil and 1.7 billion long tons of sulphur (Webber and Warne 1979).

Most of the industrial emissions of sulphur are in the form of sulphur dioxide. Most of its gets accumulated in the soil system through dry and wet deposition and plant residues. Wet deposition is mostly due to the action of rain and snow. Dry deposition mechanisms involve gravitational settling, turbulent and Brownian diffusion, electrical and photosynthetic effects.

1.2 SORPTION BY SOILS

It has been known for many years that soils and clay minerals have the ability to sorb atmospheric gases. Sameshima and Hemmi (1934), measured the sorption of sulphur dioxide by zeolites and bentonites and found the sorption at one atmospheric pressure for different minerals ranged from 1 to 70 mL of sulphur dioxide per gram of clay. Alway et al. (1937) exposed samples of surface soil in the field for one month and found sorption of sulphur dioxide. Fuhr et al. (1948) exposed 13 ft.^{2} of soil which contained 11% moisture to an atmosphere containing 5000 to 10 000 mg SO_2/m^3 for one hour. They found that all of the sulphur dioxide had disappeared after 40 minutes. Dick and Walker (1975) and Krouse et al. (1977) measured sulphur deposition over the summer months near sulphur extraction plants and reported about 2.5 kg/ha. Barrie and Welpdale (1977) conducted a study of sulphur deposition in the oil sands plant in February 1976. They reported a maximum sulphur deposition of about 4 $kg \cdot ha^{-1} \cdot yr^{-1}$. Johansson (1959) set out bare potted soils downwind at a distance of 1 to 8 km from a sulphur dioxide source for six years. The ratio of sulphur gained by the soil through direct sorption from the air to that gained through precipitation ranged from 2 to 7, depending on the site. He noticed a drop in soil pH between 0.3 to 1.4 units. In Ontario, Cox (1975) set containers of three soils under canopies downwind from two sulphur dioxide emitting smelters. At a distance of 15 to 25 km from the emission source, the pH of the top 1 cm of a silty clay loam dropped 0.2 to 0.4 units after 19 weeks exposure and soluble sulphate content of the soil increased by 17 to 70 ppm. Nyborg et al. (1977) reported that a soil kept in containers at four sites downwind from a large SO_2-emitter in southern Alberta gained from 12 to 53 kg S/ha in 3 months, and most of this gained sulphur was not found as soluble sulphate. In addition, Nyborg et al. (1980) found that another soil gained an average of 48 kg S/ha after four months, when the soil was kept in containers protected from rain at six sites downwind (> 30 km) from a group of large SO_2-emitters in central Alberta. Little of the gained sulphur was found as sulphate sulphur. Hsu and Hodgson (1977) obtained generally similar results with a soil set out in central Alberta with the sites 6 to 15 km from SO_2-emitters.

Numerous laboratory experiments have demonstrated that soils have a large capacity for the sorption of sulphur dioxide (Abeles et al. 1971). Bremner and Banwart (1975) studied the rate of sorption of different sulphur gases by air-dry and moist soils in a sealed bottle by injecting 500 ppm (v/v) of different sulphur gases. They have shown that adsorption rates and capacities of both air-dry and moist soils were considerably less for CH_3SCH_3, CH_3SSCH_3, CS_2, COS as compared to H_2S, SO_2 and CH_3SH. Smith et al. (1973) showed that the average capacities of five soils to sorb SO_2 was 9.8 mg of SO_2 per g of soil when dry, and 37.8 mg of SO_2 per g of soil when moist. The greater sorption of SO_2 with moist soil, rather than with dry soil, has also been shown by Terraglio and Manganelli (1966) and Cox (1975). The rate or the extent of SO_2 sorption was not closely correlated with soil pH, soil organic matter content, or soil clay content. In addition, they concluded that soil organisms were not greatly involved in the sorption. Yee et al (1975) have demonstrated the high capacity of calcareous soils to sorb SO_2.

Ghiorse and Alexander (1976) found that sulphur dioxide was rapidly removed from the gas phase by both sterile and non-sterile soil and concluded that viable microorganisms are not directly involved in its removal from the atmosphere. In both sterile and non-sterile soil, about one quarter of the sulphur introduced as sulphur dioxide could not be recovered as sulphite or sulphate. Recovery was quantitative however if the soil was first ignited to destroy organic matter. They concluded that 25% of the total missing sulphur might have been bound in the form of organic sulphur.

1.3 PURPOSES OF THIS INVESTIGATION

One of the purposes was to determine in the field the amounts of sulphur gases which were sorbed by a bare, moist soil protected from rain, in the vicinity of two large gas plants emitting sulphur dioxide. In addition, any concomitant uptake of nitrogen in the soil was to be determined. The other purpose was to find, in the laboratory, the rate of SO_2 sorption by soils and the effect on the soils.

2. MATERIALS AND METHODS

2.1 FIELD EXPERIMENT

The soil was similar to the cultivated Gray Luvisol that is described with the several soils used in the laboratory experiment. This soil was air-dired and crushed to pass a 2 mm sieve. The soil was placed in 1-L plastic open-topped containers 12 cm in depth. At each site, two replicated containers full of the soil were set out from June to September (3½ months). Each two weeks the soils were watered (with distilled water) to 0.33 atm. moisture content. The containers sat on a 0.5 m high shelf in shelters and a 1.2 m high wooden roof (without walls) kept natural rain from the shelters.

There were shelters at eight locations in the vicinity of two large natural sour gas processing plants, and two distant locations were used as controls. While the locations were in a forest, the shelters were generally set in clearings.

2.2 LABORATORY EXPERIMENTS ON SO_2 SORPTION

2.2.1 Soils

Four soils were used, two cultivated soils and two litter layers of coniferous forests. The samples were taken from the 0-15 cm depth, air-dried and crushed to pass a 2 mm sieve. (The soils will be described in Table 3).

2.2.2 Procedures

The reaction vessels used to study gas sorption by soils were 1000 mL flasks fitted with air-tight 24/40 ground-glass female joints with a 2 mm Teflon stop-cock attached to the side of the flask.

These stop-cocks were gas tight, fitted with a small, needle-puncture rubber septum that allowed injection of a gas sample by a gas syringe. The Teflon stop-cock was immediately closed after injecting a known amount of sulphur-dioxide to avoid the sorption of SO_2 by the rubber septum.

To study the sulphur dioxide sorption by soils, a known amount of the test gas was injected into a sealed 1000 mL bottle containing a known weight of air-dry soil (2 mm size) or air-dry soil adjusted to 0.33 atmosphere moisture content by addition of water. The amounts of injected sulphur dioxide were such that 400 or 200 μg of SO_2-S were supplied per gram of soil. After fifteen minutes the stopper was removed and the soil was transferred to a loosely covered plastic container awaiting analysis.

In another experiment the same procedure was followed except the 200 μg of SO_2-S per gram of soil was added as 40 increments of 5 μg of SO_2-S per day over a period of 40 days keeping the time of reaction to 15 min/d. The sorption experiments were performed at room temperature ($22^{\circ}C$), and all injections of sulphur dioxide were performed with Pressure-Lok gas syringes supplied by Precision Sampling Corporation. The sulphur dioxide used was obtained from the Matheson Corporation.

2.3 SOIL ANALYSES

Soil pH was determined with a glass electrode (soil:water ratio, 1:2.5 in mineral soil and 1:25 in organic soils), organic matter by wet oxidation (Walkey-Black method), particles size analysis by the hydrometer method, total nitrogen by the macro-Kjeldahl method and cation exchange capacity by NH_4OAC at pH 7. Extractable ammonium and nitrate was made by the method of Bremner (1965).

Total sulphur was measured by the alkaline oxidation method (Tabatabai and Bremner 1970) using a bismuth reagant (Dean 1966) with the Johnson and Nishita (1952) method.

Extractable sulphate was measured by shaking 10 g of soil with 20 mL of 0.1M $CaCl_2$ for half an hour, taking 2 mL of filtrate and determining the SO_4-S according to Tabatabai and Bremner (1979), and Johnson and Nishita (1952), using a modified end point (Dean 1966).

3. RESULTS AND DISCUSSION

3.1 FIELD EXPERIMENTS

The detailed analyses for sulphur and nitrogen of the soil, which was set out for a 3½ month period is shown here for only one of the control sites and one of the sites exposed to SO_2 emissions (Table 1). A high concentration of nitrate occurring only in the 0-1 cm depth is surprising, but the mineralization of nitrate is to be expected as the soil lay bare and moist. The net increase in mineral N throughout the 0-12 cm depth was similar at the two sites, 17 and 20 kg N/ha, at the control site and the SO_2-exposed sites (Table 2). The soluble-sulphate sulphur content scarcely increased during the period in which the containers were kept out of the eight sites. This is exemplified by the two sites shown in Table 2. On the other hand, the soil at the SO_2-exposed site had acquired about 60 kg/ha of non-sulphate sulphur in only 3½ months. It is also surprising that the non-sulphate sulphur, to a degree, segregated itself from layer to layer in its concentration in the soil (Table 1). This variation roughly showed as differences in N:S ratios. In soils that are low in soluble-sulphates (like this one) one expects the nitrogen: sulphur ratio to be fairly stable because this ratio reflects the entire nitrogen and sulphur contents of the organic matter of a soil.

Table 1. The chemical characteristics by depths of the same soil kept in containers from June to September under canopies at one site exposed to SO_2 emissions and at another control site.

Site	Depth (cm)	N (ppm)		S (ppm)		Total N:	SO_4-S		NH_4-N		NO_3-N		Soil pH
		Total	σ*	Total	σ*	Total S	ppm	σ*	ppm	σ*	ppm	σ*	
Control	0-1	760	16	125	7	6.1	4.8	0.1	4	ND	111	ND	5.72
	1-3	714	0	103	4	6.9	2.4	0.1	3	ND	9	ND	5.86
	3-5	714	0	67	1	10.7	1.8	0.1	2	ND	6	ND	5.84
	5-12	672	25	73	4	9.2	1.9	0.0	2	ND	7	ND	5.86
Exposed	0-1	790	25	123	9	6.4	5.2	0.1	4	ND	106	ND	5.53
	1-3	655	17	102	2	6.4	2.0	0.1	3	ND	14	ND	5.86
	3-5	656	33	108	2	6.1	1.9	0.0	3	ND	8	ND	5.83
	5-12	696	25	133	5	5.2	1.7	0.0	2	ND	7	ND	5.80

*σ = standard deviation for Total N, Total S, and Extractable SO_4-S.

Table 2. The amounts of N and S (expressed as kg/ha) found in soil when the soil was the original unexposed sample; samples kept in 12 cm-deep containers open to the air at a site free of SO_2 emissions; and samples kept in 12 cm-deep containers open to the air at a site exposed to SO_2 emissions. The soil in the containers was periodically moistened.

Identical sub-samples of the soil	kg/ha					Total N: total S
			Extractable			
	Total N	Total S	SO_4-S	NH_4-N	NO_3-N	
Original	1125	143	3.3	9	6	7.9
Control site	1160	138	3.8	4	28	8.2
SO_2 exposed site	1145	201	3.7	4	31	6.0

The soil pH values were lower for the SO_2-exposed site than the control site only in case of the 0-1 cm layer (Table 1). Usually in this type of field work with soils held in containers, there is a minimum of soil pH variation from replicate to replicate and site to site. Any depression of soil pH after a season is statistically significant only when considering soil samples from a group of sites together. It is noted that Nyborg et al. (1980) found that for three poorly buffered cultivated soils, kept in containers for three months at 52 sites, the soil pH in the 0-5 cm layer was lower by 0.1 units when the sites were SO_2- exposed as compared to the control sites.

Figure 1 displays the values for non-sulphate sulphur gained at the eight sites near to the two plants. The eight sites, in the vicinity of the two gas plants, were set within an area of 30,000 ha, and the average value for gain of non-sulphate sulphur was 62 kg/ha in the summer season. (It may be of interest that the "maximum design capacity" of sulphur emission was more than 120 long tons per day for the two plants taken together).

A second soil exposed in the same manner gave only 23 kg/ha of gain of non-sulphate sulphur. The other results for this second soil are not given because of experimental variation, but the soil tended to become sealed on the surface with water and was very acid. The first soil was very porous to air or water.

Fowler's (1980) work points out that near SO_2 sources the dry deposition is much greater than wet deposition, and the characteristics of the soil surface (pH, roughness, the amount of water) greatly matters to the rate of deposition velocity of SO_2. However, our field work is complicated by containers of soils placed above the ground and the presence of shelters with their covering rooves, and the placement of most shelters in clearings. Nevertheless, the large amount of sulphur taken in by the soil in our experiment (and by another soil in open country in Central Alberta, as reported by Nyborg et al., 1980) was almost all non-sulphate sulphur and that is important to the understanding of what occurs in the reaction between soil and SO_2.

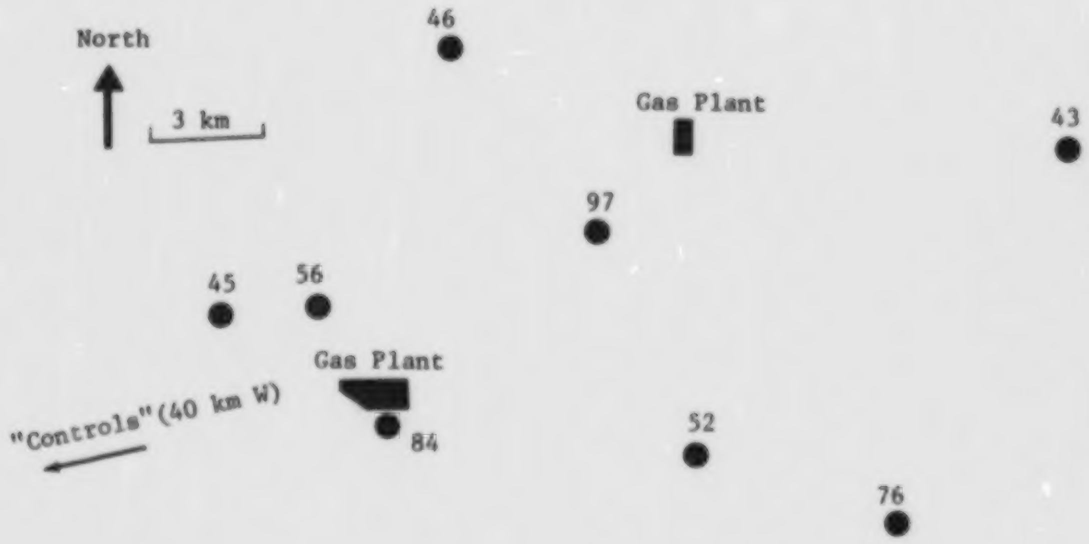
North
3 km
46
Gas Plant
43
97
45
56
Gas Plant
"Controls"(40 km W)
84
52
76

Figure 1. Gain of non-sulphate sulphur in June to September by a bare moist soil protected from rain but open to the air. The statistical standard error of the mean is 4.3 kg/ha on non-sulphate S.

3.2 LABORATORY EXPERIMENTS ON SO_2 ADSORPTION

3.2.1 Soils

The four soils used in these experiments are tablulated in Table 3. The two cultivated soils were lower in soil organic content and coarser in texture than are most of the cultivated soils in the Province. That is, these two soils were rather poorly buffered. The two organic soils were acid, and they were from litter layers under a forest. The sample "Organic-I" consisted partly of fresh mosses and fallen needles, and the material in sample "Organic-II" was partly decomposed.

3.2.2 First Experiment

Air-dry samples of the four soils were placed on the floor of separate 1-L erlenmeyer flasks. SO_2 was introduced into the flasks and the flasks were held sealed for 15 minutes then opened and the soils removed. The weight of the soil samples were 50 g for the cultivated soils and 5 g for the organic soils. The rate of addition of sulphur dioxide-sulphur added to the soil was 400 µg of S in the gas per 1 g of soil.

The treatment with SO_2 of each of the four soils was the same when considered on the basis of weight to weight, but the resultant treatments were quite different among soils on the weight to volume basis. That is, the estimated bulk density of the four soils in the field to a depth of 15 cm was 1.3, 1.2, 0.5, 0.01, for the Gray Wooded, Dark Gray, Organic-I, and Organic-II, respectively.

The soil pH values with an without the SO_2 treatment of the Gray Wooded soil were 4.54 and 6.20, respectively. In the same order, pH values were 5.24 and 6.64 for the Dark Gray soil; 4.19 and 4.32 for the Organic-I soil; and 3.57 and 3.85 for the Organic-II soil. When the estimated bulk density of the soils were taken into consideration, the rate of application of SO_2-S in the field (into the top 15 cm of the soils) for the soils were 840, 720, 30 and 60 kg S/ha.

Table 3. Some characteristics of the experimental soils.

Soil name	Description	Texture	Silt (%)	Clay (%)	Soil organic matter (%)	Total N (%)	pH	Total S(ppm)	SO_4-S (ppm)	Cation exchange capacity (m.e./100g)
Gray Wooded	Cultivated; Gray Luvisol	SL	18	12	1.4	0.11	6.3	91	5	6.4
Dark Gray	Cultivated; Dark Gray Chernozem	L	38	14	3.8	0.16	6.6	157	5	12.1
Organic I	Forest, litter layer					1.13	4.3	1720	400	64.8
Organic II	Forest, litter layer					1.19	3.8	1850	125	91.5

These simple results are unusual in showing that these four diverse, and thoroughly air-dried soils, were acidified by a short-term treatment with SO_2 gas. The determination of pH values was repeated after the samples were stored without hermatically sealing, and results were similar.

Preliminary sulphur analyses were made on the samples and apparently the majority of the applied SO_2 was retained by the soils, most of it as sulphate-sulphur but some as non-sulphate sulphur.

3.2.3 Second Experiment

An experiment with the two cultivated soils was conducted with a rate of SO_2-S at 200 μg/g of the soil. There were two treatments, with the soils kept air-dry, as compared to the soils kept at 0.33 atm. moisture content. In two more treatments, the SO_2 was all applied in a single 15-minute period, as opposed to small doses of SO_2 applied at 15-minute periods for each of 40 days. The retention of the applied SO_2 was essentially complete when the gas was added during the 40-day period, on the basis of total sulphur determinations of the soils (Table 4). Even with the one 15-minute dose, the recovery was better than 80%. The soil samples, moist or air-dry, on the treatment with SO_2 behaved much the same judging by total sulphur, sulphate-sulphur, and the non-sulphate sulphur. We did not expect the formation of non-sulphate sulphur in the soils without much regard to the soil moisture or length of treatment.

The acidification of the soils by the SO_2 took place across all of the treatments (Table 5).

The rate of treatment of our two soils with SO_2 probably fell far short of the capacity of soils to sorb SO_2 as reported by Smith et al. (1973). Our purpose in this small experiment was only in determining the effect of SO_2 on soil pH, and on the formation of non-sulphate sulphur in the soil. The formation of non-sulphate sulphur in soils from SO_2 treatment has been little studied or recognized. We have preliminary results suggesting that most of this sulphur can be found in the hydroiodic acid-reducible fraction of the soil sulphur.

Table 4. The gain in SO_4-S and total S content of two cultivated soils with and without treatment with SO_2 at a rate of 200 µg of S per 1 g of soil. Soils were treated with 200 $\mu g \cdot g^{-1}$ in one 15- minute period, or else 5 $\mu g \cdot g^{-1}$ in 15-minute long periods in each of 40 days.

Soil name	The moistness of soil; the length of time exposed to SO_2	The gain in S content on SO_2 treatment		
		Total S (ppm)	Sulphate S (ppm)	Non-sulphate S by difference (ppm)
Gray Wooded	Dry; 15 minutes	179	98	81
	Dry; 40 days	212	122	90
	Moist; 15 minutes	166	90	76
	Moist; 40 days	198	128	70
Dark Gray	Dry; 15 minutes	163	128	35
	Dry; 40 days	190	154	36
	Moist; 15 minutes	165	132	33
	Moist; 40 days	200	148	52

Table 5. The pH of two cultivated soils with and without treatment with SO_2 at a rate of 200 μg of S per 1 g of soil. Soils were treated with 200 $\mu g \cdot g^{-1}$ in one 15-minute period, or else 5 $\mu g \cdot g^{-1}$ in 15-minute long periods in each of 40 days.

Soil name	The moistness of soil; the length of time exposed to SO_2	Soil pH after treatment	
		No SO_2	SO_2
Gray Wooded	Dry; 15 minutes	6.26	4.90
	Dry; 40 days	6.26	4.66
	Moist; 15 minutes	6.06	4.93
	Moist; 40 days	6.06	4.95
Dark Gray	Dry; 15 minutes	6.64	5.63
	Dry; 40 days	6.64	5.47
	Moist; 15 minutes	6.25	5.65
	Moist; 40 days	6.25	5.42

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TESTING FOR VEGETATION GRADIENTS IN THE ATHABASCA OIL SANDS AREA

E.C. PIELOU[1]

ABSTRACT

It is known that air pollution from the Athabasca oil sands exhibits concentration gradients along the Athabasca River valley. Concentrations decrease both northward and southward from SUNCOR. A search was made to determine whether there were corresponding gradients in the species-composition of ground vegetation in the valley. The vegetation in mature balsam poplar stands was chosen for investigation because of its uniformity.

The test for vegetation gradients consists of: (1) listing the species in each of a row of sampling sites along the suspected gradient; (2) constructing an ordered similarity matrix (OSM) whose elements are the pairwise similarities (Sorensen's Index) between every pair of samples; (3) computing the "disarray" (number of reversals) in the OSM, and comparing the observed value with that expected under the null hypothesis of no gradient.

Application of the test showed that there is at present no evidence of pollution-caused gradients in the vegetation of balsam poplar stands in the oil sands area.

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1. INTRODUCTION

Prolonged, severe air pollution is known to have a marked effect on the species-composition of affected vegetation. A classic, well-documented example was given by Gordon and Gorham (1963). They observed the number of plant species in a sequence of sample plots at successively greater distances from the iron-sintering plant at Wawa, Ontario and found that species number increased with increasing distance from the pollution source. The effect was conspicuous and the conclusion indubitable.

In regions of low intensity air pollution, vegetation changes are likely to be far more subtle, and hence harder to detect. This paper describes a test for the existence of minor changes in species-composition along a pollution gradient. The test was applied to data collected in the Athabasca valley above and below the SUNCOR oil sands plant; it was found that the vegetation examined shows no sign of pollution-caused change at present.

2. THE STATISTICS OF ORDERED SIMILARITY MATRICES

Imagine a monotonic environmental gradient, trending north-south, say. Suppose a row of n sampling sites is located along the gradient, and the species-composition of the vegetation is observed at each site. Let an ordered similarity matrix (OSM) be constructed: this is a symmetric $n \times n$ matrix whose (i,j)th element is a measure of the vegetational "similarity" between sites i and j. Any appropriate similarity measure may be used. In the example described in Section 4, the similarity measure is Sorensen's index (described below).

The pattern of an OSM contains much information about the trend (if any) in the vegetation. Three examples (artificial) are shown in Figure 1 to illustrate the discussion. Because of its symmetry around the principal diagonal, only half of each OSM is shown. To make the patterns conspicuous, black circles have been put in the cells: the larger the circle in any cell, the closer the similarity between the two sites whose similarity is entered in that cell. Clearly, the OSM in Figure 1a indicates a "perfect" vegetation

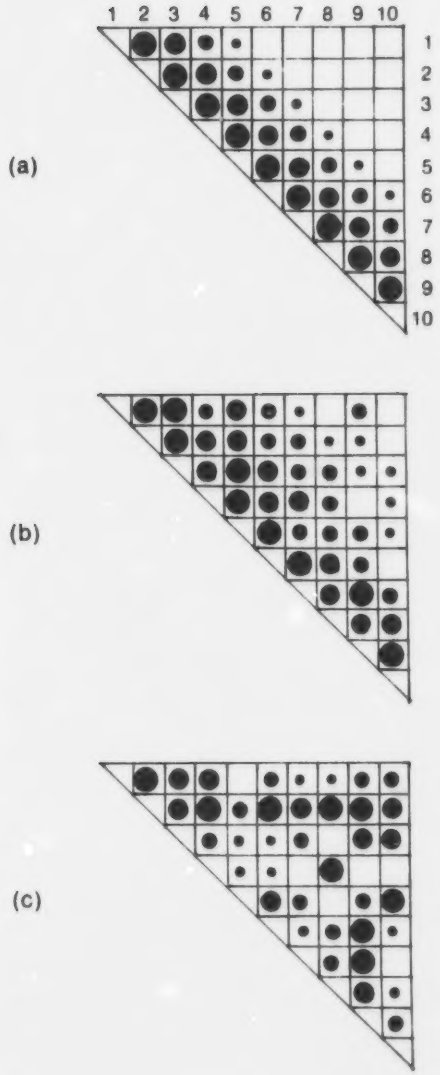

1 2 3 4 5 6 7 8 9 10
1
2
3
4
5
6
7
8
9
10
(a)
(b)
(c)

Figure 1. Three 10 x 10 OSM's (artificial) to illustrate some possible forms.

gradient: the similarity between any pair of immediately adjacent sites (one step apart) is greater than that between any pair two steps apart; these latter similarities are greater than those between any pair of sites three steps apart; and so on. The OSM in Figure 1b, judged intuitively, gives evidence of a fairly good, but not perfect, trend. The OSM in igure 1c shows no evidence of any trend at all, implying that the vegetation sampled lacks any north-south trend in composition.

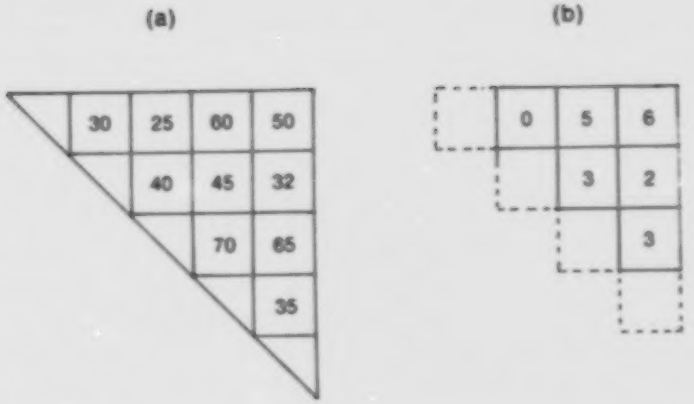
It is easy to envisage OSM's falling between 1b and 1c for which it would not be obvious on inspection whether or not they portrayed a trend. Therefore, we now consider a means of testing such OSM's in order to decide whether to accept or reject the null hypothesis that there is no trend.

To perform a test, it is necessary to devise some quantitative measure of what may be called the "disarray" of an OSM. Such a measure, denoted by Q, is described in Pielou (1979, 1982). For a perfectly ordered matrix like that in Figure 1a, $Q = 0$. That is, the disarray is zero when every element (similarity coefficient) in the OSM exceeds all the elements in all "higher" diagonals. (The diagonals higher than a given diagonal are those lying farther from the principal diagonal, hence nearer to the northeast corner, than the given diagonal.) When any element is less than an element in a higher diagonal, the pair of elements exhibit a "reversal". Q is the sum total of all reversals in an OSM. A numerical example of the computation of Q is shown in Figure 2, in which numerical similarity coefficients are shown in the cells of a 5 x 5 OSM, with elements s_{ij}; the matrix of reversals m_{ij} gives, in each cell, the number of reversals of which the corresponding s_{ij} is a member.

The maximum possible value for Q, say Q_m, depends on n, the number of sites sampled. It is obtainable from the recurrence relation $Q_m(n+1) = Q_m(n) + n^2(n-1)/2$ with $Q_m(4) = 11$.

If the vegetation at the sequence of sites being examined is wholly free of trend (equivalently, if the OSM is "random" as in figure 1c) the sampling distribution of Q is symmetrical with

$$E(Q) = Q_m/2.$$



An ordered similarity matrix, $\{s_{ij}\}$

The corresponding matrix $\{m_{ij}\}$, showing numbers of reversals

$$Q = \sum_i \sum_j m_{ij} = 19$$

Figure 2. To illustrate the computation of Q.

(a) A 5 x 5 OSM; its elements, s_{ij}, are similarity indices.

(b) The matrix of reversals; each element m_{ij} is the number of elements (in the OSM) less than s_{ij} in lower diagonals.

Therefore Q/Q_m, which must lie in the interval [0, 1], is a useful test statistic for judging the acceptability of the hypothesis that an OSM is trend-free. Figure 3 (adapted from Pielou, 1982) shows the critical region for a 5% test. For the relevant n, any observed value of Q/Q_m may be entered on the graph. If it falls in the critical (shaded) region, below the curve, the null hypothesis of "no trend" may be rejected at the 5% significance level (one-tailed). Otherwise it should be accepted. (The points marked, N, S, and W are described in Section 4).

3. MONOTONIC AND REVERSING GRADIENTS

Thus far, attention has been focused on monotonic gradients. Now consider gradients such as those radiating from a pollution source. There will (in simple cases) be a gradient of decreasing pollutant concentration along lines radiating from the source, which is a singular point. A single straight line, with the singular point at or near its centre, exhibits what will be called a reversing gradient: the monotonic trends on each side of the singular point are in opposite directions.

Now envisage a series of 12, say, sampling sites, ranged in a north-south row and labelled, in order, 1, 2, ..., 6, 6', 5', ... 1'. The pollution source is located at the centre, between sites 6 and 6'. If two separate OSM's were to be constructed, one for sites 1, ..., 6 and the other for sites 6', ..., 1', it might be found that both gave evidence of a trend in vegetation composition (see Figure 4a and 4b). However, consideration of the two separate OSM's would not suffice to show that pollution was the cause of the observed trends. To decide this point, it would be necessary to construct the OSM for all 12 sites taken together. Then two possible outcomes are conceivable (see Figure 4c and 4d). If the trends shown by the two 6 x 6 OSM's were due, not to pollution, but to some overriding, monotonic north-south environmental gradient, then the combined (12 x 12) OSM would be of the form of Figure 4c, indicative of a monotonic trend in vegetation composition. But if, on the contrary, pollution were indeed the cause of the trends in the two six-site sequences, the combined OSM would be of the form of

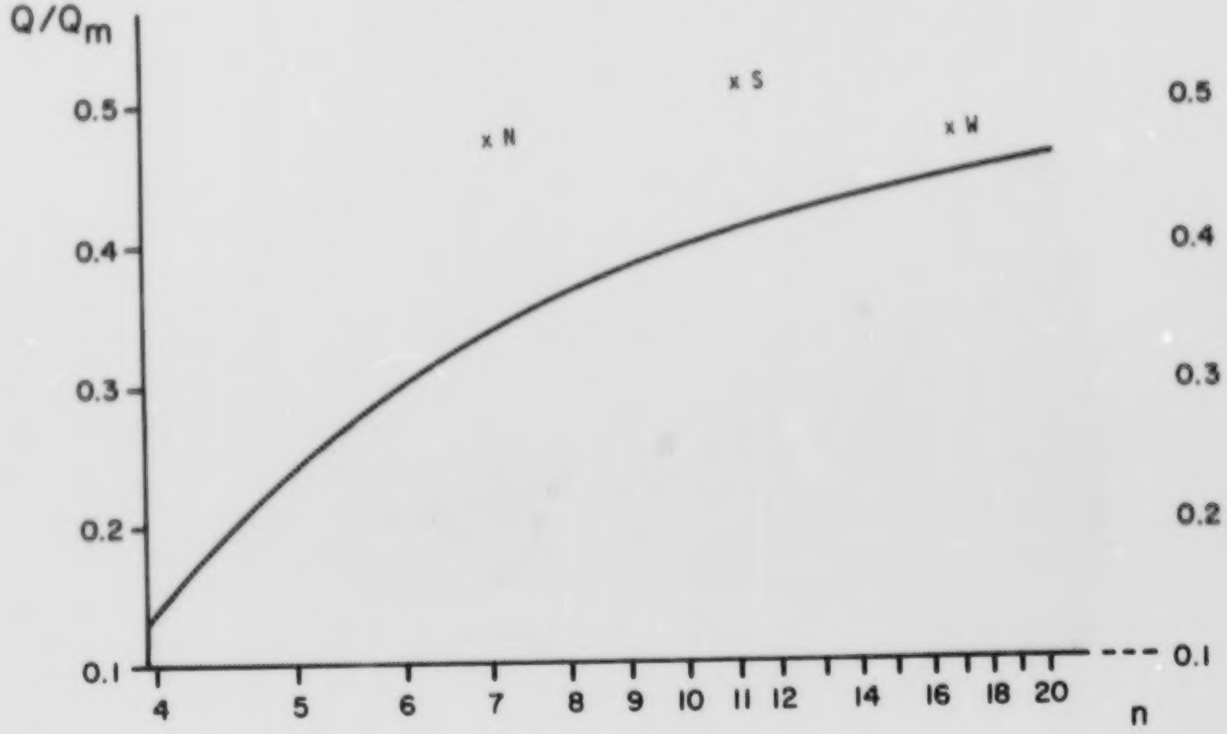


Figure 3. The curve shows the 5th percentile of the distribution of Q/Q_m as a funtion of n, the number of sites sampled. To do a 5% test, enter the observed $(n, Q/Q_m)$ on the graph. If it falls below the curve, reject the null hypothesis of no gradient. The points W, N, and S are for the OSM in Figure 6 and subsets of it; details in text. (Redrawn from Pielou, 1982)

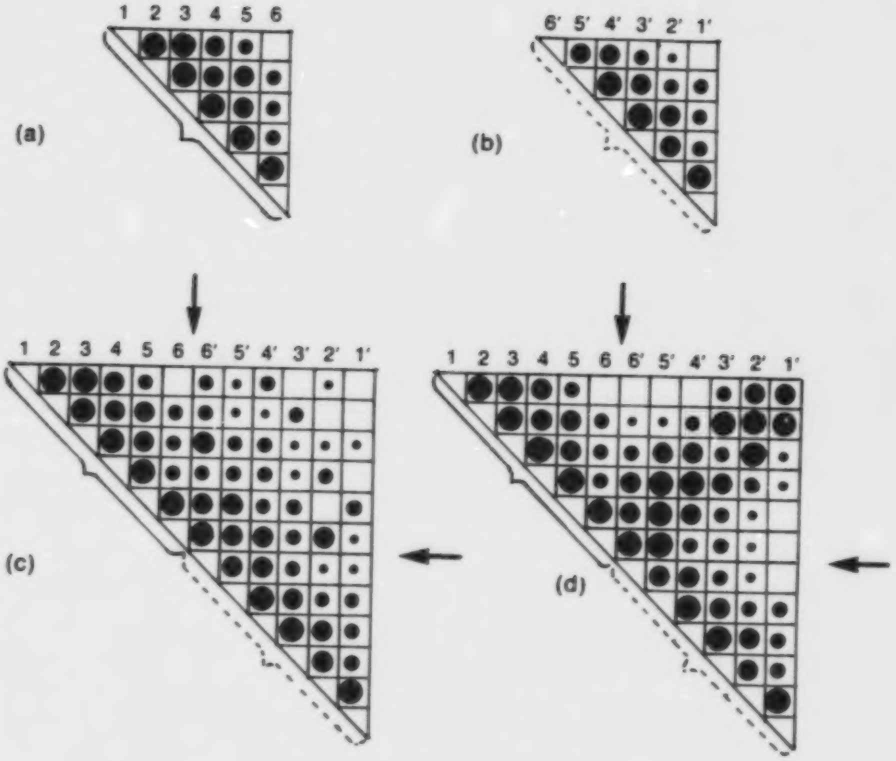

1 2 3 4 5 6
(a)
6' 5' 4' 3' 2' 1'
(b)
1 2 3 4 5 6 6' 5' 4' 3' 2' 1'
(c)
1 2 3 4 5 6 6' 5' 4' 3' 2' 1'
(d)

Figure 4. OSM's from monotonic and reversing gradients. Both the small OSM's (a) and (b), based on six sites which end at a singular point, show trends. The large OSM's show two possible outcomes of treating all twelve sites (assumed to be co-linear) together; (c) indicates a monotonic gradient; (d) indicates a reversing gradient that changes direction at the singular point (arrow).

Figure 4d in which the similarity coefficients are high on both diagonals. Notice that the two small OSM's are embedded in the large ones.

It is straightforward to test the hypothesis that an OSM represents a monotonic gradient against the alternative that it represents a reversing gradient. There are $n(n-1)/2$ cells in an OSM; it is easy to devise formal rules for dividing the cells into two groups that are respectively, close to, and far from, the diagonals. Then the values of the similarity coefficients in these two groups of cells can be compared using a Mann-Whitney test.

4. APPLICATION OF THE TEST TO OIL SANDS VEGETATION

The test described above was used to determine whether there are any trends in the species-composition of the ground vegetation in the Athabasca oil sands area that could be attributed to air pollution.

Various studies of the pollution pattern in the area have been made. For example, Strosher (1977) presented maps showing total sulphation isopleths, and H_2S isopleths, averaged over various periods, at a time when SUNCOR (previously GCOS) was the only oil sands plant operating. Barrie and Kovalick (1978) mapped wintertime deposition of pollutants. And Addison and Puckett (1980) mapped the quantities of sulphur, vanadium and aluminum in corticolous lichens in the region. These maps all suggest that pollutants are funnelled along the valley of the Athabasca river. From Addison and Puckett's maps it appears that sulphur concentrations decrease northward and southward from a maximum in the neighborhood of the SUNCOR plant.

The probable existence of a pollution gradient along the Athabasca valley guided the search for trends in vegetation. It was decided to locate sample plots, in a row along the valley, in vegetation as uniform in composition as possible. Stands of mature *Populus balsamifera* proved to be the most suitable sites as there was very little variation among them. Unlike uplands forests that are frequently burned, or *Populus tremuloides* stands that suffer sporadic tent caterpillar infestations, stands of *P. balsamifera* usually have a comparatively uncheckered history. They appeared to vary among themselves only in signs of recent spring flooding. The stands chosen for sampling were those where no sign of flooding were evident.

Seventeen such stands were found. Their locations are shown in Figure 5. At each of them, a 200 x 200 m plot was established. Within the plot, 25 1 m^2 quadrats were systematically located and the species in each quadrat were recorded. A total of 53 species was found in all 17 plots combined, and they are listed in the appendix.

The data were used to construct a (53 x 17) presence-absence matrix, from which was derived a (17 x 17) OSM showing the similarity between every pair of plots. This OSM is shown in Figure 6. Sorensen's index was used as similarity coefficient. It is defined as $2x/(2x+y)$, where x is the number of species common to the two plots concerned and y is the number of species found in one but not both plots. A coefficient calculated from presence-absence data was preferred to one (such as percent similarity) based on measured quantities of the different species, since it gives more weight to uncommon species. These are presumably less hardy than the abundant species and hence, perhaps, more likely to be affected by pollution.

There is no obvious sign of trends in the OSM in Figure 6. Tests were done separately for the northern and southern segments of the row of plots, and also for the row as a whole. The resultant values of Q/Q_m are plotted in Figure 3.

For the 7 northern plots (i.e. from the northernmost plot, #1, to and including #7, across the river from SUNCOR)
$Q = 82.5$. When $n = 7$, $Q_m = 175$ whence $Q/Q_m = 0.471$.
(See point N in Figure 3).

For the 11 southern plots (from the southernmost, #17, to and including #7)
$Q = 1320$. When $n = 11$, $Q_m = 660$, whence $Q/Q_m = 0.500$.
(See point S in Figure 3).

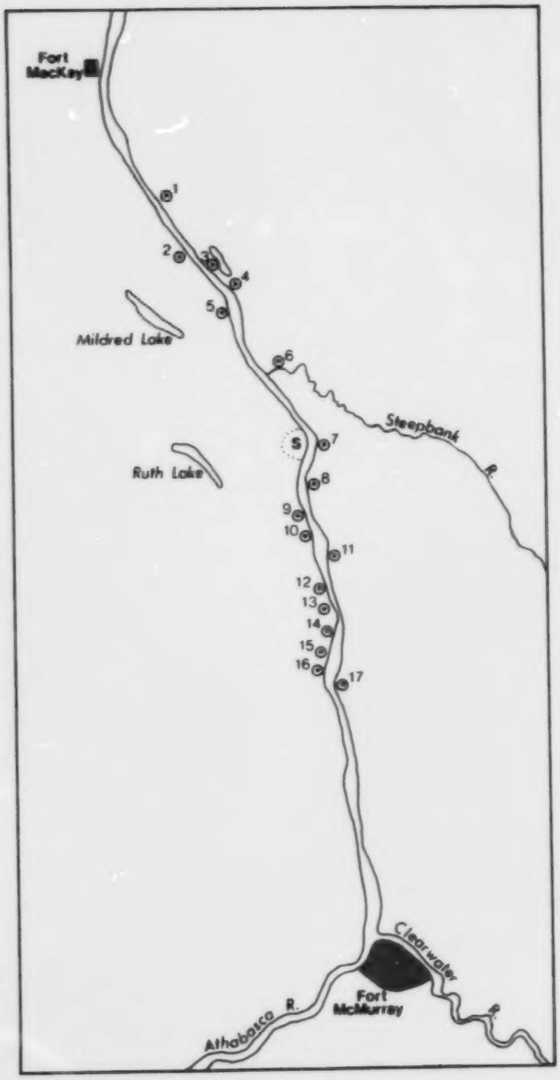

Fort MacKay
1
2
3
4
5
Mildred Lake
6
Steepbank R.
S
7
Ruth Lake
8
9
10
11
12
13
14
15
16
17
Clearwater R.
Fort McMurray
Athabasca R.

Figure 5. Map showing the locations of the 17 sample plots. S is the location of SUNCOR.

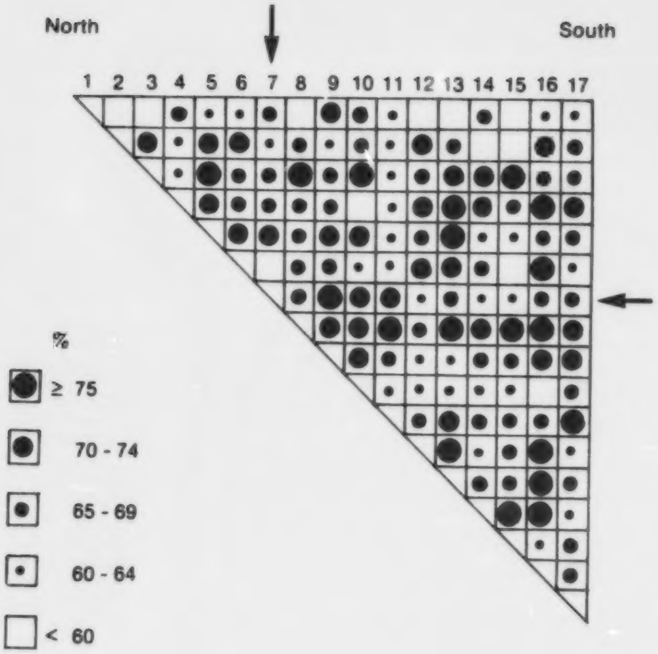


Figure 6. The OSM for the 17 observed plots in the Athabasca River valley. Plot #7, marked with arrows, is the plot nearest SUNCOR.

For the whole row

$Q = 3988$. When $n = 17$, $Q_m = 8500$, whence $Q/Q_m = 0.469$.
(See point W in Figure 3.)

Since all points fall in the acceptance region for a 5% test, there are no grounds for rejecting the null hypothesis that the vegetation sampled is devoid of trends in species-composition.

ACKNOWLEDGEMENT

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APPENDIX

The following is a list of the 53 plant species found at all 17 sampling sites. Nomenclature follows E.H. Moss, "Flora of Alberta", University of Toronto Press, 1977.

In all 17 sites: *Populus balsamifera, Cornus stolonifera, Viburnum* spp*, *Ribes triste, Rubus strigosus, R.pubescens, Mertensia paniculata.* (*Mostly *V.edule;* possibly some *V.trilobum* also.)

In 16 sites: *Equisetum pratense, Galium triflorum.*

In 15 sites: *Ribes oxyacanthoides, Calamagrostis canadensis.*

In 13 sites: *Rosa acicularis, Aralia nudicaulis.*

In 12 sites: *Prunus virginiana, Mitella nuda.*

In 11 sites: *Maianthemum canadense, Thalictrum venulosum.*

In 10 sites: *Alnus tenuifolia, Actaea rubra, Galium boreale.*

In 8 sites: *Symphoricarpos albus, Circaea alpina.*

In 7 sites: *Viola rugulosa.*

In 6 sites: *Amelanchier alnifolia, Lonicera dioica, Stellaria longifolia.*

In 5 sites: *Matteucia struthiopteris,* unidentified grass sp, *Cornus canadensis, Vicia americana, Stachys palustris, Pyrola asarifolia, Aster* sp.

In 4 sites: *Picea glauca, Ribes americanum, R.glandulosum, R.hudsonianum, Smilacina stellata, Scutellaria galericulata.*

In 3 sites: *Abies balsamea.*

In 2 sites: *Rhamnus alnifolia, Adoxa moschatellina.*

In 1 site: *Populus tremuloides, Salix* sp, *Carex deweyana, Urtica gracilis, Stellaria longipes, Ranunculus macounii, Anemone canadensis, Fragaria virginiana, Heracleum lanatum, Trientalis borealis, Erigeron acris.*

SULPHUR IN FORESTS: AN APPLICATION OF ECOLOGICAL MONITORING

A.H. Legge[1], J.C. Bogner[1]

ABSTRACT

The objective of this paper is to present one aspect of the results of an ecological monitoring program carried out in the West Whitecourt study area from 1976 to 1980 as an extension of the West Whitecourt Case Study. The approach taken in the study was to repeatedly measure the foliar sulphate-sulphur concentration in lodgepole x jack pine foliage at ecologically analogous sampling locations (A_I-A_V) over five growing seasons (1976-1980), relate this foliar concentration to sulphur (S) gas emissions from the AMOCO Canada Limited West Whitecourt Gas Plant, and determine if foliar sulphate-sulphur concentration could be used as a practical ecological indication of sulphur loading of the forest ecosystem on a routine basis.

A pronounced increase in foliar sulphate-sulphur was detected at A_I-A_{II} in 1980. In two-year old foliage this corresponded to an increase at A_I from 532 ppm in 1979 to 1027 ppm in 1980, and an increase at A_{II} from 574 ppm in 1979 to 752 ppm in 1980. The majority of this increase in foliar sulphate-sulphur concentration was not attributed to S gas emissions but to sulphur dust originating from the Texasgulf Sulphur Limited sulphur granulation operation which commenced production on 26 June 1979. Microbial breakdown of the elemental sulphur dust in the soil by species of the genus *Thiobacillus* has resulted in the production of H_2SO_4. A portion of the $SO_4^=$ produced was taken up by the trees as it passed through the root zone. It is predicted that soil acidification and disruption of mineral nutrient cycling in the forest ecosystem has occurred, at least at A_I and A_{II}. Foliar sulphate-sulphur is seen as a practical indicator of sulphur loading of the forest ecosystem. The magnitude and kinetics of sulphur assimilation and sulphur accumulation by forest ecosystems warrants further investigation.

The ecological analogue concept has provided the necessary theoretical foundation and site selection criteria for comparable sample site selection when designing a terrestrial ecological monitoring program. The application of the ecological analogue concept to other areas of the province of Alberta is clearly practical.

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1. INTRODUCTION

The principal source of sulphur (S) gas emissions in Alberta is the sour gas processing industry. The potential environmental impact in Alberta from these emissions has been a major concern of this industry since the early 1970's. One major expression of this concern was a five year environmental research program called the Whitecourt Environmental Study carried out between 1972 and 1976. This program was cooperatively financed by an industry consortium called the Whitecourt Environmental Study Group (WESG) formed in 1971, the Oil Sands Environmental Study Group (OSESG), and the Alberta government. The industry consortium consisted of eight petroleum companies having operations in the Whitecourt district of west-central Alberta. The objective of the Whitecourt Environmental Study was to determine the environmental consequences of the operation of 11 sour gas processing facilities on the forest ecosystem in west-central Alberta.

No large scale environmental disturbances, however, were detected in the first two years of the Whitecourt Environmental Study, so a case study was initiated in 1974 near the AMOCO Canada Petroleum Company Limited West Whitecourt (Windfall) sour gas processing plant to investigate small-scale environmental disturbances. This gas plant was chosen for two main reasons:

1. It had the longest operational history of the 11 gas plants in the Whitecourt study area dating back to 1961-1962; and
2. There was small scale visible evidence in the vegetation of environmental stress from S gas emissions.

The objective of the West Whitecourt Case Study was to determine the consequences of chronic exposure of the forest ecosystem to low concentrations of S gas emissions originating from the West Whitecourt Gas Plant. The results of this study have been summarized by Legge (1980) and Legge et al. (1981).

One of the important discoveries during the course of the case study was the determination that the foliar sulphate-sulphur concentration in *Pinus contorta* Loud. x *Pinus banksiana* Lamb. (lodgepole x jack pine) tissue provided an excellent indication of exposure of the forest ecosystem to sulphur (S) gas emissions originating from the West Whitecourt Gas Plant. The question which remained unanswered, however, was whether or not foliar sulphate-sulphur concentration in lodgepole x jack pine trees could provide a useful ecological monitoring tool which would be indicative of sulphur loading of the forest ecosystem in the long term?

The role of sulphur as an essential plant nutrient and the controversy arising when more sulphur is available than can be assimilated has been summarized by Legge (1980). When more sulphur is available than can be assimilated as organic sulphur by a plant, it is accumulated as inorganic sulphur (sulphate-sulphur) in the plant tissue. It must be borne in mind that both processes are going on simultaneously. In this paper the terms sulphur loading and sulphur accumulation are used interchangably.

The objective of this paper is to present one aspect of the results of an ecological monitoring program carried out in the West Whitecourt study area from 1976 to 1980 as an extension of the West Whitecourt Case Study. The approach taken was to repeatedly measure the foliar sulphate-sulphur concentration in lodgepole x jack pine foliage at preselected ecologically analogous sampling locations over five growing seasons (1976 to 1980), relate this foliar concentration to S gas emissions from the West Whitecourt Gas Plant, and determine if foliar sulphate-sulphur concentration could be used as a practical biological indication of sulphur loading of the forest ecosystem on a routine basis in Alberta.

2. SULPHUR GAS EMISSION HISTORY

It is essential to characterize the source in terms of emissions to the atmosphere in an air pollution based ecological monitoring program as thoroughly as possible. These data when combined with the local and regional meteorological factors provides the potential input of pollutant to the ecosystem. Although the West Whitecourt Gas Plant commenced operations in 1961 to 1962, a complete record of the S gas emissions history is only available since 1967.

The yearly S gas emission output history of the West Whitecourt Gas Plant from 1967 through 1980 is shown in Figure 1. Total S emissions in long tons (LT) per year represents the summation of all S emissions for each year from both the incinerator stack and the flare stacks. The 78% reduction in yearly total S gas emissions, over the fourteen year period of record, from 33 098 LT/year in 1967 to 7 274 LT/year in 1980 is significant.

The S gas emission sources must be further characterized. However, from an environmental viewpoint, it is the time of year as well as the concentration, duration and frequency with which S gas emissions enter the atmosphere that are the main emission factors determining the environmental consequences upon the terrestrial ecosystem, and not simply the total S gas emissions emitted per year.

The S gas emission output history of the AMOCO West Whitecourt Gas Plant for January 1970 through December 1980 therefore is shown in Figure 2. Total S emission in long tons (LT) per month represents the summation of all daily S emissions for each calendar month from both the incinerator stack and flare stacks. The pronounced March/April 1976 drop in total S emissions represents the initial effect of the start-up of a tail-gas recovery unit.

Each S gas emission source type--incinerator stack and flare stacks--is discussed separately in terms of time and output. The total monthly output of each of these sources in long tons (LT) is shown in Figure 2 to illustrate the relative contribution of each source type to the total combined S emissions. These output figures are further broken down into mean S emission output per day through each calendar month for both source types. The variability in S emission output of each source type is shown as the range around the mean daily S emission output which occurred for each source type in each calendar month rather than by the more conventional standard deviation around the mean. This is important in the case of the flare stacks because they are discontinuous S gas

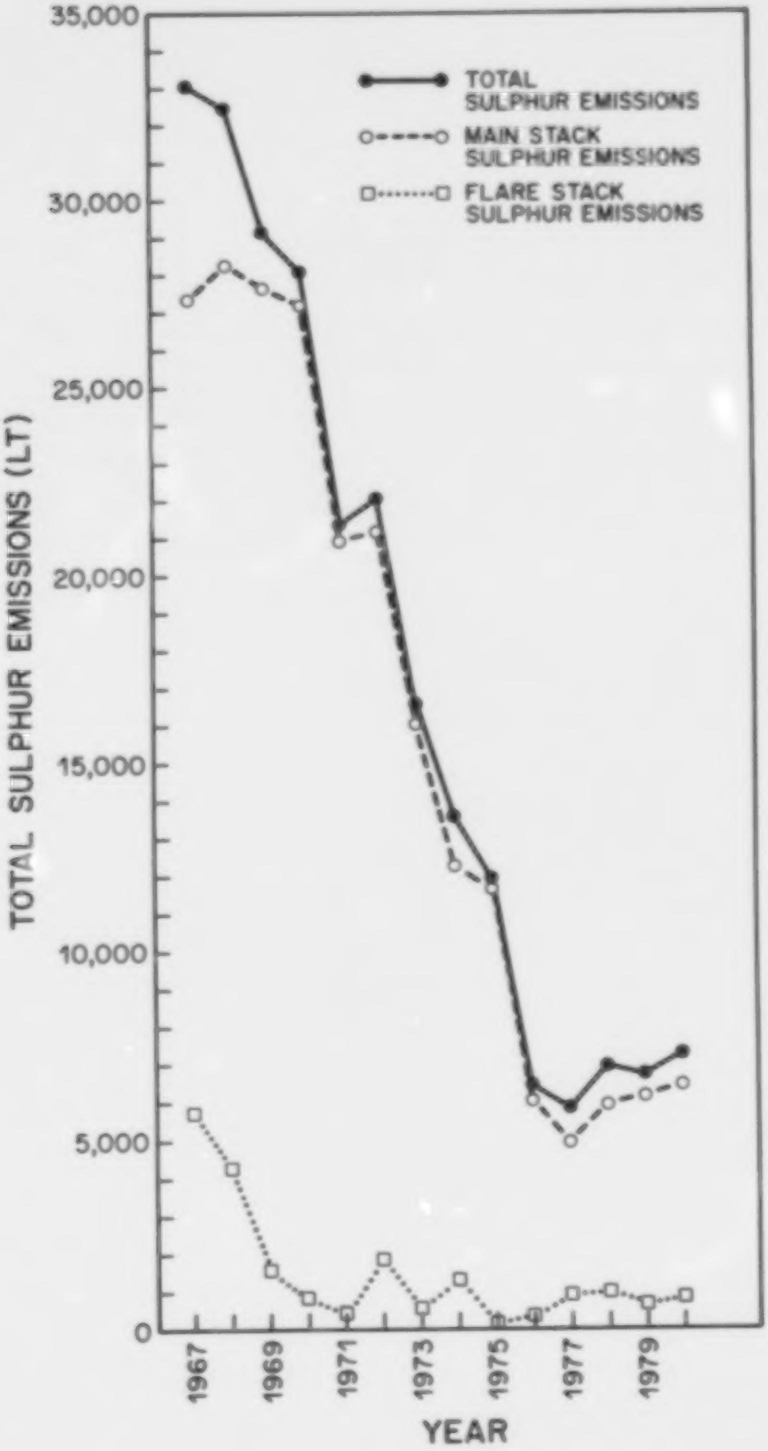

Figure 1. Yearly S emission output history in long tons (LT) of the West Whitecourt Gas Plant from 1967 through 1980.

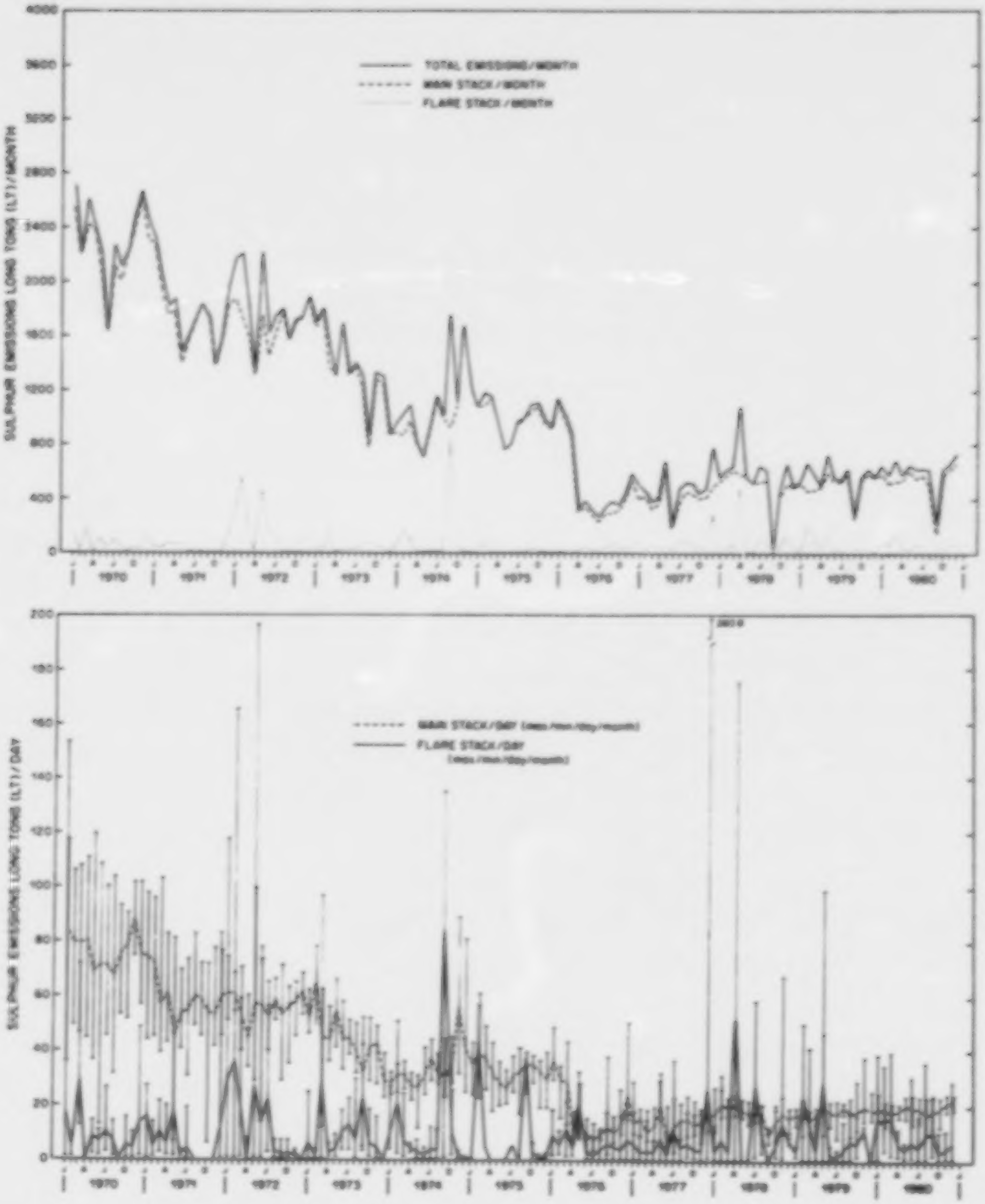

Figure 2. Monthly sulphur emission output history in long tons (LT) of the West Whitecourt Gas Plant from January 1970 through December 1980.

emission sources. The mean S emission value per day during each month for each source type is based upon the number of gas plant operating days per month for the incinerator stack and the number of days in a given month when measurable flaring occurred at the flare stacks. These data are based upon incinerator and flare stack monitoring records from the West Whitecourt Gas Plant.

It is clear from Figure 1 that the incinerator stack contributes most of the S gas emissions to the atmosphere on a monthly and daily basis. However, during a gas plant operating upset, the flare stacks can contribute substantially more S emissions to the atmosphere on a daily basis than the incinerator stack does under normal operating conditions. An extreme example of this type of flaring occured on 9 December 1977 when 235.8 LT was flared during a single day. In contrast, mean daily incinerator stack emissions for the month of December, however, was only 16.5 ± 2.6 LT.

It is important to make the following observations with regard to S gas emissions from the West Whitecourt Gas Plant to assist in the interpretation of the foliar sulphate-sulphur concentration data obtained during the six-year period 1975 through 1980:

1. Mean yearly incinerator stack S gas emissions decreased from 32.7 LT in 1975 to a low of 11.4 LT during 1976, after the addition of the tail gas recovery units in April 1976. Since 1976 however, mean yearly incineration stack S gas emissions have been gradually increasing and reached 18.6 LT in 1980;
2. In terms of the seven month active growing season (April through October) total S emissions from the incinerator stack decreased from 6 596 LT in 1975 to 2 102 LT in 1976, but then began increasing to 2 878 LT in 1977, 3 244 LT in 1978, 3 527 LT in 1979, and 3 537 LT in 1980;
3. Total yearly S gas emissions from the flare stacks have increased from the low of 160 LT in 1975 to 396 LT in 1976, 919 LT in 1977, 989 LT in 1978, 634 LT in 1979, and 815 LT in 1980; and

4. In terms of the seven month active growing season (April through October) S gas emissions from the flare stacks have increased from the low of 65 LT in 1975 to 256 LT in 1976, 394 LT in 1977, 729 LT in 1978, 260 LT in 1979, and 414 LT in 1980.

3. SAMPLE SITE SELECTION

One of the principal difficulties encountered by air pollution researchers, before collecting samples in the field for analysis, is the initial selection of sampling locations. Most sampling locations in air pollution studies are chosen solely on the basis of a gradient which is usually a function of the prevailing wind, the distance from a pollution source, and convenience. Not enough emphasis is placed upon the structure and composition of the plant communities from which samples are taken. Since an ecosystem is composed of many interrelated highly variable biological and physical components, the response of these components to a chronic environmental stress such as air pollution will also be highly variable. If the range of variability of the responses of ecosystem components to an environmental stress is not considered, the expression of the effect of the environmental stress such as air pollution on the ecosystem components may not be detected. There must be a common basis for comparison of ecosystem components therefore to determine both the gross and subtle effects of an environmental stress along a gradient.

The concept and criteria for ecologically analogous sample site selection were developed and applied during the West Whitecourt Case Study in an attempt to minimize the variability of ecosystem components and hence to minimize the variability of the response of the ecosystem components to air pollution stress. The key to this concept of sample site selection is based upon comparable ecological variability of the ecosystem components and comparable environmental variability at the sampling locations chosen along a distance gradient. When the ecological and environmental variation of ecosystem components at all the sampling locations are as similar as possible, the sampling sites are said to be ecologically analogous.

The criteria for ecologically analogous sample site selection were developed during the West Whitecourt Case Study and are summarized in Figure 3 (Legge et al. 1981). The major difference among the sampling locations therefore is distance from the pollution source. The assumption is that the pollutant variables such as concentration, frequency of fumigation and duration of fumigation will decrease in magnitude with increasing distance from the pollution source. The magnitude of the air pollution stress on ecosystem components at the sampling locations will correspondingly decrease with increasing distance from the pollution source. This procedure ensures that the expression of the air pollution stress on ecosystem components will be maximized.

Five ecologically analogous lodgepole x jack pine sampling locations were selected in the West Whitecourt Case Study area, and are shown in Figure 4. The five sample sites were chosen in locations which were progressively downwind in the main path of the S gas emission corridor. These sites were chosen in this manner so that the S gas emission impact gradient would be very steep across the five sampling locations to maximize the differences in the responses of the ecological analogues to pollution stress.

The ecologically analogous sampling sites were located at distances of 1.2 km (A_I), 2.8 km (A_{II}), 6.0 km (A_{III}), 7.5 km (A_{IV}), and 9.6 km (A_V) from the gas plant. Sampling locations in the study area other than ecological analogues were designated by the letter S. Sampling location S_o in Figure 4 is 13.0 km from the gas plant and was chosen for reference purposes.

4. METHODS AND MATERIALS

4.1 FOLIAGE SAMPLE COLLECTION

Foliage samples were collected after each growing season from five different lodgepole x jack pine trees at each of the six sampling locations (A_I to A_V, and S_6) shown in Figure 4. The

ECOLOGICAL ANALOGUE CONCEPT

ASSUMPTIONS $1 \equiv 2 \not\equiv 3$

1. Ecological Variables (sites $A_1 \rightarrow A_n$)
   - slope
   - aspect
   - soil type
   - soil moisture
   - species density
   - species diversity
2. Environmental Variables (other than pollutants)
   - temperature
   - wind
   - solar radiation
   - precipitation
3. Pollutant Variables
   - composition
   - location
   - distance
   - concentration/conversion
   - frequency/duration

$$[SO_2]_{A_1} > [SO_2]_{A_2} > [SO_2]_{A_3}$$
$$> [SO_2]_{A_4} > [SO_2]_{A_5} \cdots > [SO_2]_{A_n}$$

Figure 3. Summary of criteria utilized for the selection of ecologically analogous sample locations.

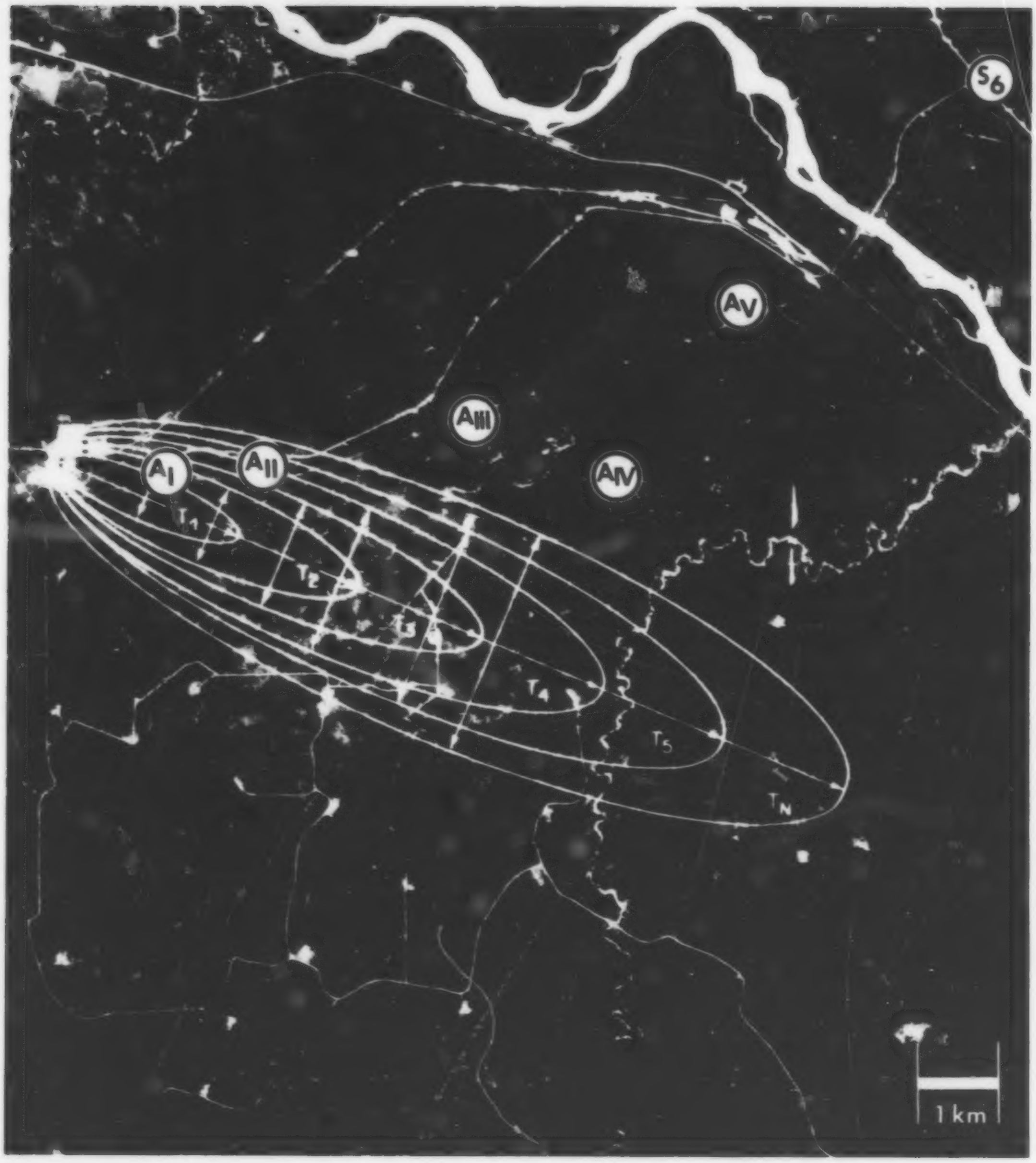

Figure 4. Black and white aerial photograph showing the location of the six lodgepole x jack pine foliage sampling sites in the West Whitecourt study area near the West Whitecourt Gas Plant in west-central Alberta. All sample locations are shown in relationship to the prevailing direction of the wind, WNW⇌ESE. The aerial photograph originated from color-infrared imagery acquired 11 August 1976 at an original scale of 1:120 000. (Canada Center for Remote Sensing Roll A373621R Frame #130)

mean age of all the trees in 1976 was 29 years. The foliage samples were harvested from the top portion of each of the trees on the side facing the West Whitecourt Gas Plant using a long-handled tree pruner. The foliage samples from each tree were tagged, placed in large plastic bags, and transported to the Kananaskis Centre for Environmental Research (University of Calgary) at the end of each collecting trip. Upon arrival at the laboratory, all the foliage samples were recorded in a lab book and then frozen. The foliage samples were frozen as soon as possible after collection to avoid the increases in foliar sulphate-sulphur noted by Handreck (1971) when foliage was stored fresh.

Foliage samples were collected at the following times between growing seasons: 18 September 1976 (1976), 17 October 1977 (1977), 17 January 1979 (1978), 5 April 1980 (1979), and 18 January 1981 (1980). The growing season sampled is shown in brackets. The purpose in collecting foliage samples at different times between growing seasons was to determine the months of the year when physiological activity of the trees was low enough to avoid significant changes in foliar sulphate-sulphur.

4.2 FOLIAGE SAMPLE PREPARATION

The frozen samples were thawed for 30 minutes prior to age-classing. Each age-classed sample was then dried at 70°C for 48 h in ventilated drying ovens. After drying, each sample was ground to a particle size of 40 mesh or less using a Wiley mill. The ground plant material was then placed in 50 mL glass bottles and dried at 36°C for 3 h to remove any moisture which may have been picked during the grinding process. The 50 mL bottles were then cooled in a desiccator until they reached room temperature before they were capped. Foliar sulphate-sulphur change during storage was minimized following this procedure.

4.3 FOLIAGE SAMPLE SULPHATE-SULPHUR ANALYSIS

Foliar sulphate-sulphur content of the ground age-classed lodgepole x jack pine foliage was determined according to the method of Johnson and Nishita (1952). A range of 3 to 300 μg of sulphur can be measured with a precision of 2 to 5%. Each foliar sulphate-sulphur concentration is the mean of three determinations on the same sample. The mean foliar sulphate-sulphur value for each sample location in 1976 is the mean of 3 trees, while in the 1977, 1978, 1979, and 1980 growing years, it is the mean concentration of 4-5 trees from each sample location.

5. RESULTS AND DISCUSSION

The mean sulphate-sulphur concentration (ppm) in age-classed lodgepole x jack pine foliage collected from six sampling locations for the growing years 1976 through 1980 in the West Whitecourt study area are plotted in Figure 5. Several general observations of these data can be made at this point:

1. There is a definite decrease in foliar sulphate-sulphur with increasing distance from the West Whitecourt Gas Plant for each of the five growing seasons sampled;
2. There has been an increase in foliar sulphate-sulphur loading at all sample locations during the past five years;
3. A pronounced increase in foliar sulphate-sulphur has been detected in all needle age classes at A_I and A_{II} in 1980, relative to other collection years; and
4. Prior to 1979 foliar sulphate-sulphur generally increased with needle-age at A_I through A_{III}, while since 1978 foliar sulphate-sulphur has decreased with needle-age.

These general observations indicate that the forest ecosystem has continued to experience sulphur loading over the past four years since the completion of field work on the West Whitecourt Case Study in 1976. Is this increase in foliar sulphate loading of the forest ecosystem due to the increase in S gas emissions from the West Whitecourt Gas Plant since 1976?

Figure 6 is a comparison of foliar sulphate-sulphur from all six sample locations as a function of needle-age and growing season collected. The decrease in foliar sulphate-sulphur with

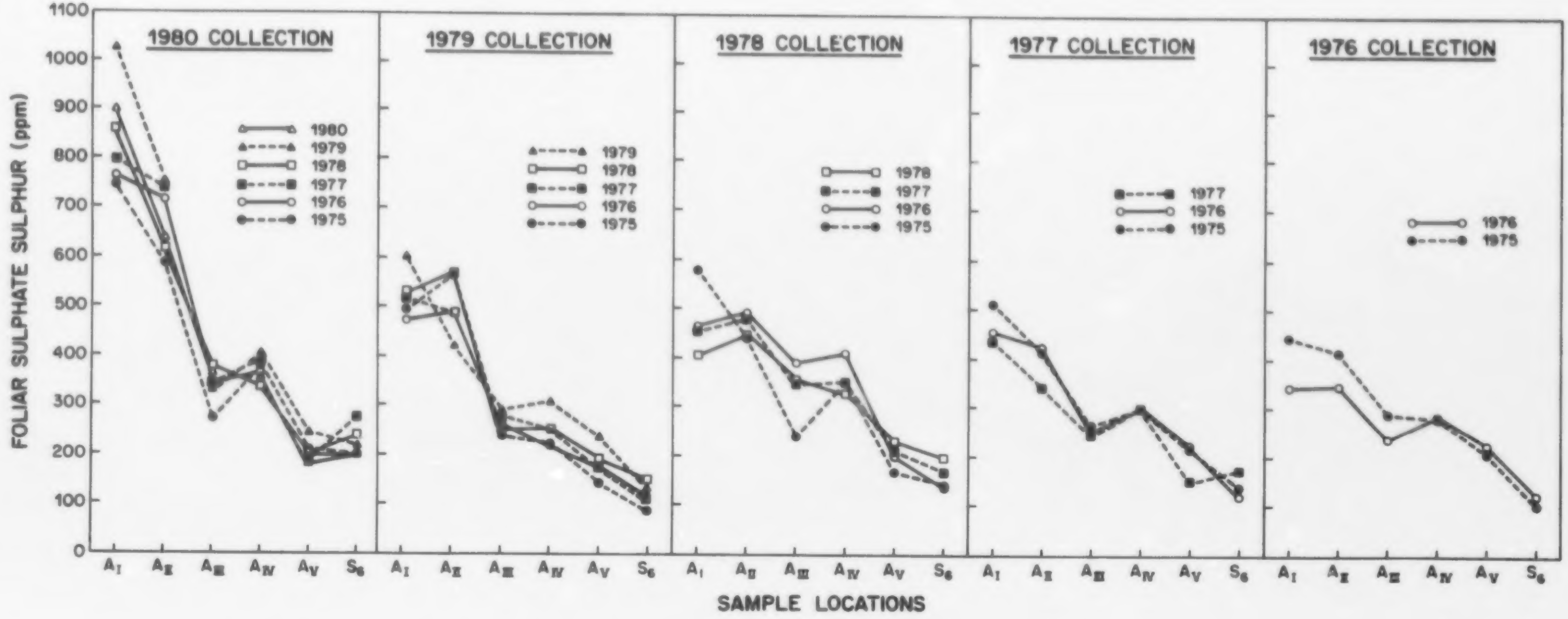

Figure 5. Summary of foliar sulphate-sulphur concentration (ppm) in lodgepole x jack pine foliage collected at sampling location A_I through A_V and S_6 on 17 September 1976, 17 October 1977, 17 January 1979, 5 April 1980, and 18 January 1981 in the West Whitecourt study area. Each of the graphs clearly show the decrease in foliar sulphate-sulphur concentration with increasing distance from the West Whitecourt Gas Plant.

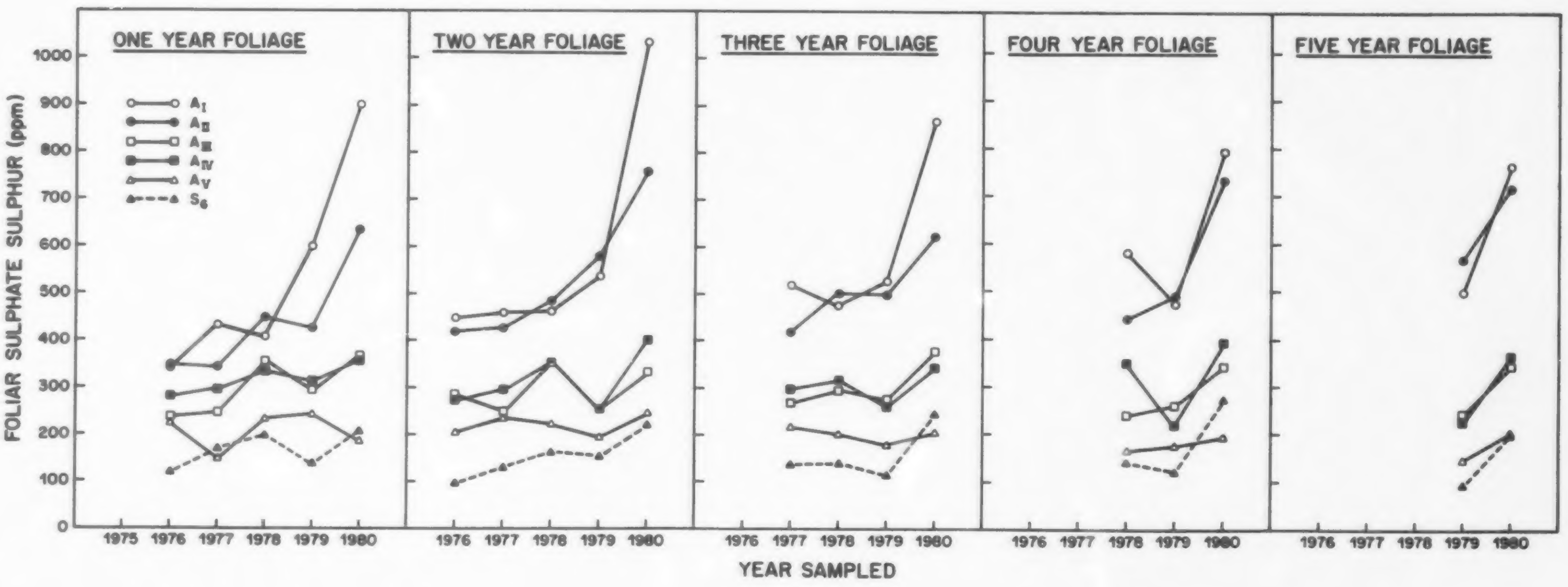

Figure 6. Comparison of foliar sulphate-sulphur concentration (ppm) in one, two, three, four, and five year old lodgepole x jack pine tissue as a function of sampling location (A_I through S_6) and growing year samples collected.

increasing distance from the West Whitecourt Gas Plant is seen again. The increase in foliar sulphate-sulphur in the 1980 collection year, however, is more pronounced when plotted in this manner. Another general observation which can be made is that the younger foliage is more efficient at accumulating sulphate-sulphur than older foliage. This is clearly seen in one, two, and three year old foliage from A_I and A_{II} when comparing 1979 and 1980 foliar sulphate-sulphur concentrations. The pronounced increase in foliar sulphate-sulphur in one year foliage at A_I, however, started in 1979. Sulphur gas emissions from the flare stacks during the seven month growing season, however, decreased in 1979 from 989 LT in 1978 to 634 LT in 1979, while the mean monthly main stack emission remained the same in 1978 and 1979. These data suggest that the foliar sulphate-sulphur increase in foliage from A_I and A_{II} in 1979 and 1980 cannot be completely attributed to S gas emissions alone.

Figure 7 illustrates foliar sulphate-sulphur loading at sample locations A_I through S_6 respectively as a function of needle-age and growing year collected. The decrease in foliar sulphate-sulphur loading with increasing distance from the gas plant is clearly documented. It is seen from this figure that A_I and A_{II} are being loaded with sulphur faster than A_{III} through S_6, and that A_{III} and A_{IV} are being loaded with sulphur at about the same rate. Although the foliar sulphate-sulphur concentrations at A_V and S_6 are low, there are indications that the foliage at these two sampling locations are beginning to load with sulphur.

From the foregoing figures and discussions in this section, it is clear that the nature of sulphur loading of the forest ecosystem has changed since 1979. As can be seen from Figure 1 and Figure 2, S gas emissions do not appear to be responsible for the pronounced increase in foliar sulphate-sulphur loading during 1979 and 1980 at A_I and A_{II}. If it is not S gas emissions, what is the cause of this foliar sulphate-sulphur increase?

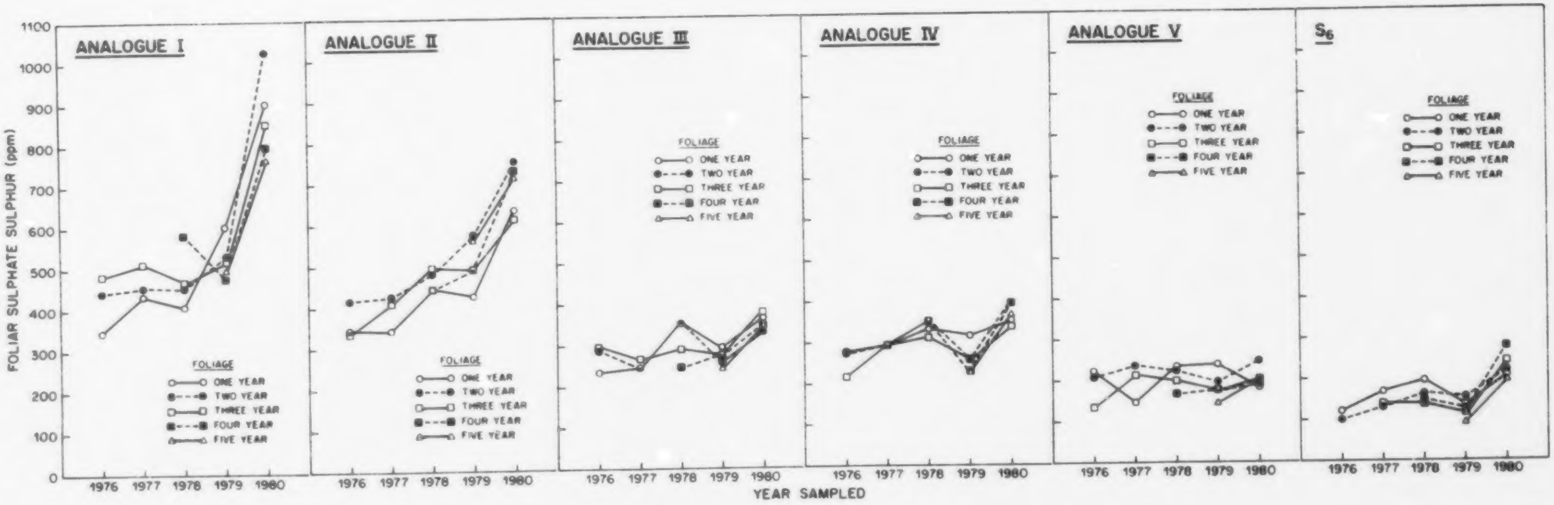

Figure 7. Comparison of the foliar sulphate-sulphur concentration (ppm) in lodgepole x jack pine foliage collected at A_I to A_V and S_6 as a function of needle-age class and growing year sampled.

On 26 June 1979, a sulphur granulation facility installed by the Sulphur Services Division, Procor Limited, commenced operation for Texasgulf Sulphur Limited adjacent to the West Whitecourt Gas Plant. The feed stock for the operation of this facility required the breaking-up of the solid block sulphur and melting of the crushed sulphur to form granules which are small solid sulphur balls. Once formed, the granules are stored in cyclindrical towers prior to transfer and shipment in Canadian National rail cars.

During the 5 to 6 April 1980 foliage sampling trip to the West Whitecourt study area, which was just prior to complete snowmelt, the granulation process at this facility was observed to be releasing sulphur dust to the environment. Sulphur dust was observed on the snow as far as 5 to 6 km from the granulation facility.

The problem with elemental sulphur in the soil environment is the production of H_2SO_4 formed by the oxidation of elemental S by species of soil bacteria *Thiobacillus* (Bryant et al. 1979). Soil acidification is a well documented phenomena near sulphur blocks. However, the same microbial process will occur as a result of sulphur dust in forest soils.

A general discussion of the rate of microbial sulphur breakdown of elemental sulphur merits consideration at this point. Populations of *Thiobacillus* in forest soils are naturally low. Once the forest soil has been "seeded" with elemental sulphur, however, the populations of *Thiobacillus* will increase in response to the sulphur food source. This process, however, takes anywhere from a number of months to years to occur, and depends not only on the surface area of the elemental sulphur but also on the soil type, soil moisture, soil temperature, and soil buffering capacity. The surface area for microbial activity, and hence the rate of elemental sulphur oxidation, is greatly increased when sulphur is in the dust form. As the elemental sulphur is gradually broken down and H_2SO_4 produced, the H_2SO_4 is leached into the soil profile. Once the $SO_4^=$ produced reaches the root zone of the

7. ACKNOWLEDGEMENTS

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lodgepole x jack pine trees, it is in a form which can be readily taken up by the trees. It is clear from increases in foliar sulphate-sulphur in the 1979 and 1980 foliage collections plotted in Figures 5, 6, and 7, that the results of this microbial activity took two growing seasons to significantly express itself. Since the soil at all the sampling locations is a degraded eutric brunisol, it is anticipated that the soil profiles at A_I and A_{II} have undergone increased acidification since 1976 (Legge et al. 1981). As a result of this acidification, nutrient cycling will have been further modified. It is important to note that sulphur dusting of the forest ecosystem from the granulation facility was significantly curtailed in the spring of 1981.

The relative contribution of sulphur dust on the forest ecosystem from sulphur-block breakup is unclear at this time. Since the particle size created during sulphur-block break-up, however, is larger than the particle size produced in the remainder of the granulation process and the release point to the atmosphere lower, gravity alone suggests that it is the latter phases of the granulation process which are responsible for the extensive sulphur dust fall-out on the forest ecosystem.

6. CONCLUSION

As a result of 5 years of foliar sulphate-sulphur monitoring in the West Whitecourt study area, it is clear from the data presented that foliar sulphate-sulphur concentration in lodgepole x jack pine tissue is a reproducible measure of sulphur loading of the forest ecosystem. These data have revealed that this is true whether the sulphur is taken up directly by the vegetation from the atmosphere as S gas emissions or indirectly through the soil as $SO_4^=$ which has resulted from the breakdown of elemental sulphur by species of the soil bacteria genus *Thiobacillus*. These data also indicate that foliage samples can be collected for sulphate-sulphur analysis from late September to late February without significant change. The 6 April 1980 sampling for the 1979 growing season was too late; the trees were just becoming active due to an early spring.

Although incinerator stack S gas emissions from the West Whitecourt Gas Plant were significantly reduced from 1967 to 1976, it is important to bear in mind that the gradual increase is S gas emissions since 1976 from 11.4 LT/day to 18.6 LT/day in 1980 was detected at the ecologically analogous sampling locations as increased foliar sulphate-sulphur. This clearly demonstrates the sensitivity of this measurement and its potential applicability in an ecological monitoring program in Alberta.

Sulphur loading of the forest ecosystem as a result of sulphur dust originating from the Texasgulf Sulphur Limited operations since 1979 is significant. These data suggest that the soils at A_I and A_{II} are being further acidified, and as a result, suggests that mineral nutrient cycling should be further modified. The data presented in this paper clearly shows that sulphur dusting of the forest ecosystem must not be allowed to occur, or the potential for irreversible ecological modification of the forest ecosystem will be increased. An evaluation of the extent of ecological modification of the forest ecosystem as a result of the extensive sulphur dusting in the West Whitecourt study area is strongly recommended.

Careful sample site selection has been shown to be essential in order to obtain the measure of ecological sensitivity to sulphur loading as evidenced by the foliar sulphate-sulphur values cited in this paper. The ecological analogue concept developed during the West Whitecourt Case Study, by Legge et al. (1981) has provided the necessary theoretical foundation and site selection criteria for comparable sample site selection. The application of the ecological analogue concept to other areas of the province of Alberta is clearly practical in an ecological monitoring program. Early warning and an adequate information base leads to an awareness of environmental problems before they get out of hand, and is the key to proper environmental management.

LUNCHEON ADDRESS

ACID DEPOSITION -A NATIONAL PERSPECTIVE[1]

J.P. BRUCE[2]

We have been fortunate to have heard a number of excellent papers yesterday and this morning on research on acid forming emissions, long- and short-range transport of air pollutants, and acid deposition in Western Canada. You'll note I used the phrase "Acid Deposition" which is much broader than "Acid Rain"--in fact, I'm reminded of this whenever I go skiing because I wear a nice red ski hat which says "Stop Acid Snow, eh."

My job here today is to try out to put this good research you've been hearing about, and acid deposition in western Canada, in some kind of national context. In fact, I would really like to try to put it into a global and continental context as well as a national one.

On a global scale, if we plot a map of mean annual pH of precipitation, we find that there are only two regions of any significant size where the pH is less than 4.5, i.e., more than ten times as acidic as clean rain. These two areas are in eastern north America, over and downwind of the industrial complex of the Midwest, Ohio Valley and southern Ontario; and in Europe downwind of the industrial heartlands of the United Kingdom, France and Germany. In these regions there are some areas where precipitation pH averages as low as 4.0 and where individual storms have values that go as low as 2.8. Where aquatic systems with little or no buffering capacity are present in these areas, we have seen the acidification of lake and river systems, the loss of fish populations and aquatic ecosystems, and the steady erosion of the remaining buffering capacity of aquatic systems.

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[1] Luncheon address

[2] Assistant Deputy Minister, Atmospheric Environment Service, Environment Canada

In eastern Canada several hundreds of lakes are now effectively "dead" due to acidification. But this is not our greatest worry. That worry is the hundreds of thousands of lakes that are dying, as we talk about it and as we do our research.

But even though these two regions are most severely affected, very few parts of the globe are entirely immune. Even in some fairly remote areas, acid precipitation from anthropogenic sources is beginning to be a concern. In Bermuda, nearly 1 000 miles from the continent, the average precipitation pH is now down to about 4.9 and individual storms take the pH down to 4.1. In the Canadian Arctic, scientists from the Atmospheric Environment Service and the U.S.A. have shown that the so-called "Arctic haze", which can seriously reduce visibility in the high Arctic, is due mainly to sulphate particles transported from Europe, U.S.S.R. and eastern North America. Scientists from the Polar Continental Shelf Project recently reported in "Nature" on their analysis of ice cores from Ellesmere Island. The bottom of the core dates back 5 000 years, but it is only in the last 25 years that a significant increase in acidity of the ice is observed.

In biological terms, the long-range transport of airborne pollutants is one more stress man is placing on the remaining species of our planet. It is estimated that of the 5 to 10 million species of life on Earth we are now losing about one per day, almost entirely due to man's activities. The most important factor is the loss of appropriate habitat in two ways:

1. Through the "mega-projects", like the huge James Bay hydro project now creating the largest lake in Quebec, flooding marshes and lowlands; and
2. Through gradual destruction of the tropical rain forest for energy supply and food production.

If we continue as we are going over the next decade or two, we can add 3 global air pollution problems to our list of environmental stresses--acid deposition, increased CO_2 beginning to cause climatic changes, and changes in the health-protecting stratopheric ozone layer by chlorofluorocarbons (CFC's) and other chemicals.

The increased acidity of lakes and streams in eastern North America have wiped out life forms in a number of aquatic systems. As a rough guide, it's been found that molluscs disappear at water pH below 5.8. Most fish disappear at water pH between 4.3 to 4.7; sponges disappear at water pH below 4.0; leeches disappear at water pH below 3.8, and zooplankton disappear at water pH below 3.7

And remember that significant areas of eastern Canada and northeastern U.S. have precipitation with pH averaging about 4.0 but with individual storms with much greater acidity. We also have very low pH runoff in spring when much of the winter's accumulation of contaminants runs off with the first melt.

But we are intelligent beings. Many of us are aware of the interdependence of species, of the importance of preventing degradation and loss of gene pools. But it seems remote and it's difficult to mobilize action.

It should be much easier to effect appropriate changes on a regional or a continental scale. Our responses so far in eastern North America and Europe have not been such as to breed great optimism; cautious optimism maybe, but not great.

One thing we have done in Canada and U.S.A. is to mobilize a major research effort. In Canada, the federal agencies are now committing $11 to 12 million per year to research on long-range transport of air pollutants and acid deposition. The provinces are spending all together another $10 to 11 million. The U.S. federal government is committing $23 million next year to acid deposition research in spite of the budget squeeze. And in Canada, we've put in place appropriate coordination machinery to get the biggest bang for the buck in research and monitoring.

Canada and U.S.A. have also signed, in summer of 1980, a Memorandum of Intent--to go beyond research. We agreed to negotiate an international agreement to control transboundary air pollution of both the short range and long range varieties. The MOI also committed each country to enforce present laws vigorously so that the situation doesn't get worse as we talk; and we committed ourselves to assemble the scientific facts of the case through bilateral scientific working groups. The reports of these working groups are the most positive achievement so far.

In the past day-and-one-half, we have heard a lot about the details of atmospheric processes, about the physical, chemical and biological complexities of acid deposition. It is a complex set of processes, but it might be helpful to pause for a minute and review in fairly simple terms what is we do know about the situation that could lead to a control strategy. The following seven points are drawn from the reports of the bilateral working groups and the past three or four years of intensive research.

1. The nitric and sulphuric acid components of acid precipitation arise largely from anthropogenic emissions of SO_x and NO_x and these have led to mean annual values of pH in precipitation of less than 4.5 over most of southeastern Canada and northeastern United States.
2. The evidence indicates that in this region the nitric acid in precipitation is largely used by the biological system and is not a major factor in affecting aquatic systems; thus control of sulphur emissions must be a first objective if we are to reduce the impacts of acid deposition on aquatic systems.
3. It is thus preferable to express an environmental target in terms of loading of sulphate to sensitive systems rather than as pH of precipitation. Such sensitive systems in eastern North America are being subjected to at least twice as much sulphate deposition as they can tolerate. This tolerable loading is estimated at an upper limit of 20 kg/ha/y of wet sulphate for moderately sensitive aquatic systems.
4. The uncertainties in atmospheric models which give the relationship between emission sources and deposition are not as great as the overload to the ecosystems, and thus they can be used to give a good indication of the major source areas affecting sensitive regions.

5. The models tell us that more than 50% of the sulphate loading in Canada comes from U.S. emissions and that 15 to 25% of the loading in northeastern U.S. is from Canadian sources.
6. Although atmospheric chemistry is complex, it is possible to consider it as a straightforward sulphur budget. Sulphur which is emitted into the atmosphere is deposited somewhere in some form, and no matter the form, it can contribute to the acidity of soils and water systems. Thus, a reduction in sulphur emissions will result in an equal reduction in sulphur deposition in its several forms in the complete downwind region.
7. The models suggest that a 50% reduction in SO_2 emissions in both eastern Canada and eastern U.S.A. would achieve, roughly speaking, a 20 kg/ha/y loading in most regions of concern.

The Canadian Environment Ministers concerned, i.e., The Hon. John Roberts, Canada, and Ministers of Ontario, Quebec, Manitoba, and New Brunswick, have accepted these scientific facts and inferences and have agreed, at a meeting last month in Toronto, to set as an initial environmental target a sulphate loading of 20 kg/ha/y of wet sulphates, and to reduce total Canadian emissions of SO_2 from the Manitoba/Saskatchewan border eastward by 50% by 1990, if the U.S.A. will carry out a parallel action.

This was the position that we on the Canadian negotiation team were directed to take to the latest session for negotiation of an air pollution agreement in Washington, February 24.

It is no secret, however, that the U.S. Administration, perhaps dazzled by the science, and unsympathetic to environmental controls, see the situation as calling for many more years of research before even initial actions can be taken. We have proposed an agreement which would provide for an initial reduction of SO_2 of, we hope, about 50% of present SO_2 emissions, and the establishment of a bilateral mechanism, perhaps the International Joint Commission or something like it, that would study the problem further and advise the two governments at a later date on further actions or modifications in controls required.

There are, of course, many things that we do not know about acid deposition and about which we wish we did know more. Two examples are the impact on soils and forests and the other is the effect of increased acidity of raw water supplies on mobilization of toxic metals in drinking water supplies.

On the forest front, the large circulation German magazine "Der Spiegel" has recently publicized widely the scientific work of Dr. Bernhard Van Ulrich in the Solling area of Germany--causing a tremendous furore there. In central and southwestern parts of West Germany, including the famous Black Forest, precipitation pH has averaged 4.1 since the sixties due to emissions in Britain, France, Belgium, and Germany. Ulrich's work shows that this precipitation has mobilized aluminum in a form toxic to the fine root hairs of trees, making them especially vulnerable to windthrow, disease, pests, etc. He claims that further natural regeneration of some species in some parts of the region is now virtually impossible. The extent to which this is happening in the Adirondacks, in central Ontario and southern Quebec, is a matter of vigorous scientific debate and investigation. At stake may be the profitability of the eastern forest industry which has net export earnings of about $4 billion per year.

On the possible human health problem, it is generally known that acidic water supplies can leach metals from sediments, rocks and pipe systems. The extent to which increased acidity of lakes and groundwater in the cottage area of Ontario is increasing toxic metal concentrations in tap water drawn from the resor lakes is under study. Reports should be available in a few months.

Thus, in eastern Canada we have a serious and worsening environmental problem of acid deposition--a problem calling for urgent remedial action to reduce SO_2 emissions. In western Canada, the situation is much more fortunate, although some local problems may exist. But for long-range transport problems, it is preventative action, rather than remedial action, that is needed.

As Alberta Environment Minister Cookson has pointed out, SO_2 emissions from Ontario are four times that from any western province.

Similarly, in the northern States west of the Mississippi River, SO_2 emissions are only 1/20th of the emissions from the northern states east of the Mississippi. International transboundary transport of acid-forming substances is a dominant characteristic of the situation in the east, but is minor in the west.

Several years ago, the provincial Environment Departments and Environment Canada agreed on three points:

1. That significant damages due to long-range transport are not likely occurring now in western Canada;
2. That there is a potential in the development of western resources and economies for emissions to reach the level where sensitive ecosystems might be adversely affected in the southern parts of Alberta, Saskatchewan and Manitoba, and in the northern parts of the North West Territories;
3. That there is a need for cooperative research and monitoring of the potential problem and for careful preventative control of SO_2 and NO_x emissions.

In order to coordinate the research and monitoring, a Consultative Committee of Deputy Ministers and senior officials was formed. A Technical Committee chaired initially by Dr. Harby Sandhu, and next year by Larry Lechner of Saskatchewan, recommends programs to the Consultative Committee and coordinates the scientific activities. The Annual Report for 1981 is now available and I would recommend it to you.

So the senior govenments in this region have by their words and actions made it clear that the price of preventing serious environmental damages will be continuing vigilance--based on sound scientific information. This conference is ample testimony to the vigour and high quality of the research efforts. To all the scientists here today--keep up the good work!

SESSION III

AQUATIC

QUANTIFYING THE SENSITIVITY OF WATER BODIES TO ACID IMPACT[1]

M. ATTON[2]

ABSTRACT

Two widely used concepts--sensitivity and impact--need more rigorous definition based on the components contributing to the aquatic ecosystem. Buffering capacity does not define lake sensitivity, just as acid loading does not define pH. Volume is an essential consideration. Lake sensitivity is one component of the sensitivity model of the ecosystem. Impact can be defined in relation to sensitivity.

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[1] This paper is available only from the author.

[2] Saskatchewan Department of Tourism and Renewable Resources.

CHEMICAL SENSITIVITY OF NORTHERN SASKATCHEWAN WATERS TO ACIDIFICATION

W.K. LIAW[1]

ABSTRACT

Total alkalinity, calcium, magnesium, and pH from some 300 freshwater bodies in Saskatchewan's Shield and fringe Shield regions were analyzed to assess the sensitivity of these lakes to potential acid precipitation. Concentrations of alkalinity in these lakes varied from 0.5 to 87 mg/L $CaCO_3$ with a mean of 18 mg/L. Forty-four percent of the lakes surveyed had alkalinity concentrations of 10 and 20 mg/L. These two groups of lakes are considered to be highly to moderately sensitive to acid precipitation.

Measurements of pH (ranging from 5.56 to 8.2) indicate that at present Saskatchewan's Shield lakes are neither very acid nor very alkaline. Lakes with pH levels between 6.5 and 7.5 accounted for nearly 80% of the lakes investigated.

Concentrations of calcium ranged from 0.33 to 31.6 mg/L with an average of 5.71 mg/L. About 54% of the lakes surveyed had calcium concentrations of 4 mg/L or less, while 25% had between 4 and 8 mg/L. Concentrations of magnesium varied from 0 to 10.7 mg/L with a mean of 1.99 mg/L. Approximately 65% of the lakes measured had magnesium concentrations of 2 mg/L or less, whereas 32% had between 2 and 3 mg/L. Concentrations of either calcium alone or calcium plus magnesium are highly correlated to concentrations of alkalinity. The regression equations are as follows (all units in μeq/L):

$$\text{Alkalinity} = 22.24 + 1.28\,(\text{Ca}) \qquad (n = 282,\ r = 0.93)$$
$$\text{Alkalinity} =-18.20 + 0.92\,(\text{Ca} + \text{Mg}) \qquad (n = 281,\ 4 = 0.97)$$

A plot of calcium concentrations versus pH for these Shield lakes in relation to Henriksen's empirical curve (1979) suggests that none of Saskatchewan's Shield lakes are being affected by acid precipitation. The data presented describe the uncontaminated conditions of Saskatchewan's Shield waters against which future changes may be evaluated.

A nomograph was constructed to depict expected rate of acidification (to the pH of 5.5), given the mean depth and alkalinity of the lake and an assumed sulphur deposition rate of 0.4 $g/m^2/y$. It is suggested that in the event of acid rain, those shallow and poorly-buffered Shield lakes in northern Saskatchewan may be acidified in a matter of a few decades.

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1. INTRODUCTION

Acidic precipitation, commonly known as acid rain, has been recognized as one of the most serious environmental threats in certain parts of the world, including eastern Canada, northeastern United States and southern Scandinavia. Precipitation in these areas is now far more acidic (pH 4.0 to 4.4) than would be expected under natural conditions. This appears to be the results of long-range transport of SO_2 and NO_x produced by the burning of fossil fuel, metal smelting, and other industrial processes (Haines 1981, National Research Council 1981). Acidification, which has lowered the pH and increased the concentrations of certain toxic metals in natural waters, affects aquatic organisms of all trophic levels, particularly fishes (Almer et al. 1978, Beamish 1976, Dochinger and Seliga 1976, Fromm 1980, Leivestad et al. 1976, Likens et al. 1979, Wright et al. 1976, Wright and Snekvik 1978). Many lakes in southern Scandinavia, southern Ontario, and northeastern U.S. have already been acidified to such critical conditions (pH <5.5) that fish populations have become very sparse or extinct. Such impacts of acid rain have not been noticed in western Canada, because the deposition of acidic sulphur and nitrogen compounds within the area is still low. However, in view of the recent and projected development of oil sands in Alberta, the probability may be high that increasing SO_2 emissions will develop into a serious ecological threat to downwind northern Saskatchewan lakes (Hammer 1980, Shewchuk 1981).

How much acid will these northern lakes be able to neutralize and how well they are able to resist pH changes depend on the ionic strength and buffering capacity of the lakes and their watersheds. In order to provide some background information, existing data of total dissolved solids (an indication of ionic strength), total alkalinity (an indicator of buffering capacity), and pH for over 600 Saskatchewan waters have been examined (Liaw and Atton 1980). On the basis of these parameters, the Precambrian Shield region in Saskatchewan has been identified as sensitive to potential acid rain. The objective of the present report was to further document and evaluate the present condition of northern Saskatchewan waters with respect to their sensitivity to potential acidification.

2. MATERIALS AND METHODS

Lakes and streams of various sizes along highways (No. 102, 105, 106, 135, 155, and 167) in northern Saskatchewan were visited at least twice during the open-water season in 1980. Water samples were collected with 2-L polyethylene bottles from the littoral zone for the determination of pH, alkalinity, hardness, calcium, and magnesium. In addition, seven lakes in the area southeast of Reindeer Lake and north of the Churchill River, and nine lakes in the region between Lake Athabasca and Cree Lake were sampled by aircraft once during August 1980. Previous measurements from other waterbodies in northern Saskatchewan were taken from Liaw and Atton (1981).

General methods used for the determination of various parameters were as follows:

1. pH: Previous measurements were mostly done in the field with a Hellige pH comparator. New measurements were made with a Fisher Accumet Model 230 laboratory pH meter, usually within 24 h after sampling.
2. Alkalinity: Old measurements were done by methly orange titration (APHA 1971). New measurements were inflection-point alkalinities by potentiometric titration. Inflection point was determined graphically or calculated by the Hahn and Weiler method. Since the fixed endpoint (methyl orange) alkalinity overestimates true alkalinity in waters of low ionic strength by approximately 32 µeq/L or 1.6 mg/L as $CaCO_3$ (Henriksen 1979), this amount was subtracted from all previous measurements of alkalinity.
3. Calcium: By EDTA titration using murexide as the indicator (APHA 1971).
4. Hardness: By EDTA titration using erichrome black-T as the indicator (EPA 1979).
5. Magnesium: Calculated from values of hardness and calcium (Environment Canada 1974); Mg (ppm) = 12.16 (total hardness as $CaCO_3$ x 0.01998 - Ca x 0.0499).

A 2-mL capacity microburet with an accuracy of 0.01 mL was used for all titrations.

3. RESULTS

3.1 TOTAL ALKALINITY

Figure 1 shows the general distribution of total alkalinity of surface waters in the Shield and fringe Shield regions and part of the sedimentary region in Saskatchewan. Concentrations of alkalinity for the 294 waters measured from the Shield and fringe Shield regions ranged from 0.5 to 87 mg/L as $CaCO_3$ (average 17.9 mg/L). Forty-four percent of these waters had alkalinities of 10 mg/L or less, 27% had between 10 and 20 mg/L, 20% had between 20 and 40 mg/L, and about 10% had more than 40 mg/L.

The distribution of alkalinities indicates that lakes and streams lying in the northern part of the Shield region usually have alkalinties of 10 mg/L or less. The waters in this part of the Shield are also very low in ionic strength with contents of total dissolved solids usually below 50 ppm (Liaw and Atton 1981). Concentrations of alkalinity of the waters that lie in the fringe Shield region, the Cluff Lake area, and the area north of Lake Athabasca were more variable. They may vary from below 10 mg/L to over 40 mg/L, but most of them were in the range of 10 to 40 mg/L. In comparison, nearly all alkalinity measurements from waters located south of the Shield in the sedimentary region were more than 40 mg/L.

3.2 pH

The general distribution of surface pH values in 305 waters from the Shield and the fringe Shield regions is shown in Figure 2. The pH ranged from 5.56 to 8.20; nearly 80% were between 6.5 and 7.5. Waters with pH greater than 7.5 were usually found in or near the fringe Shield region, the Cluff Lake area and the area north of Lake Athabasca. Following is a breakdown of the percentage of lakes in each pH catagory:

pH range	%	pH range	%
5.5 - 6.0	1.6	7.0 - 7.5	48.2
6.0 - 6.5	6.9	7.5 - 8.0	10.2
6.5 - 7.0	30.2	8.0 - 8.5	2.9

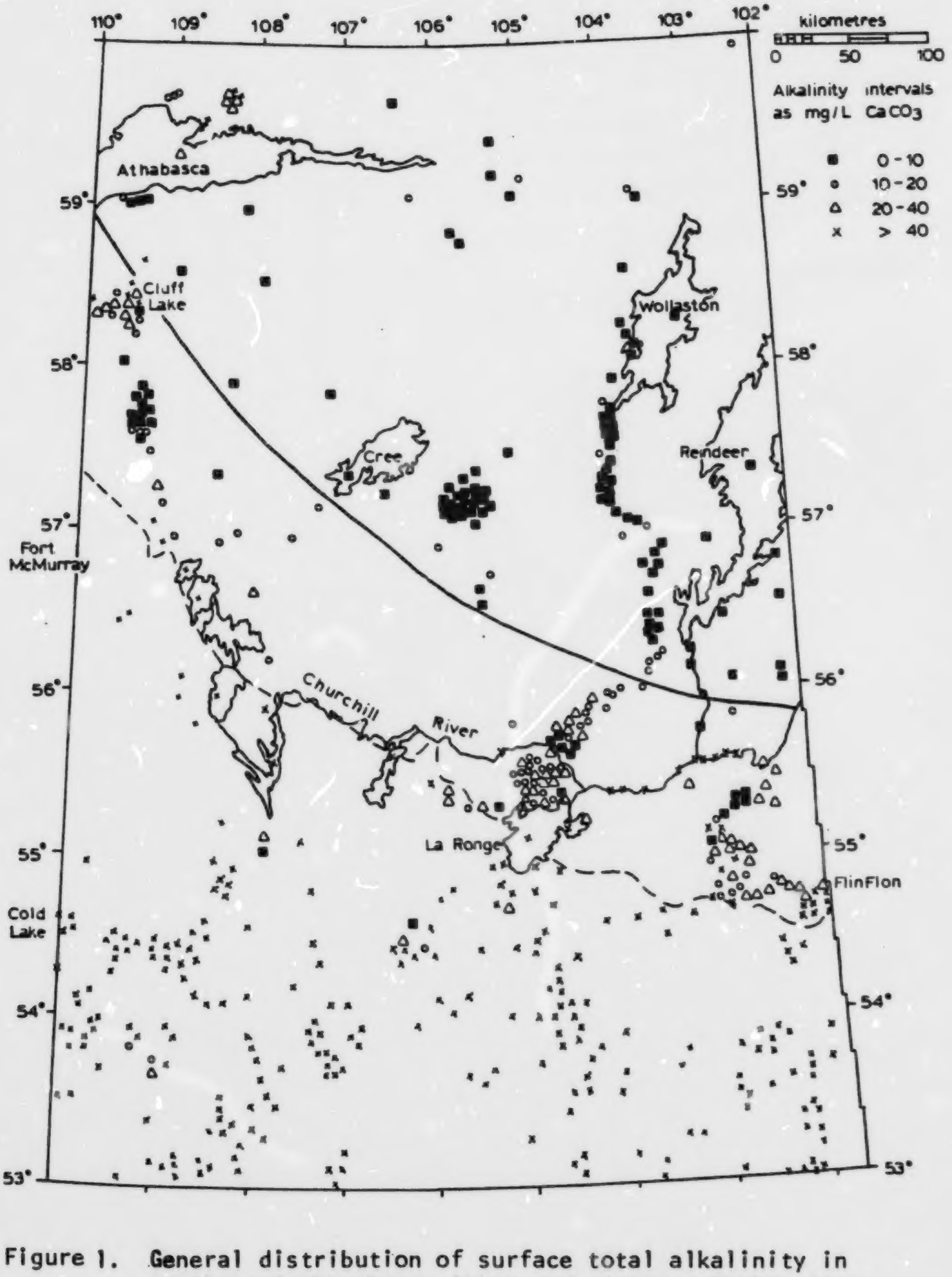
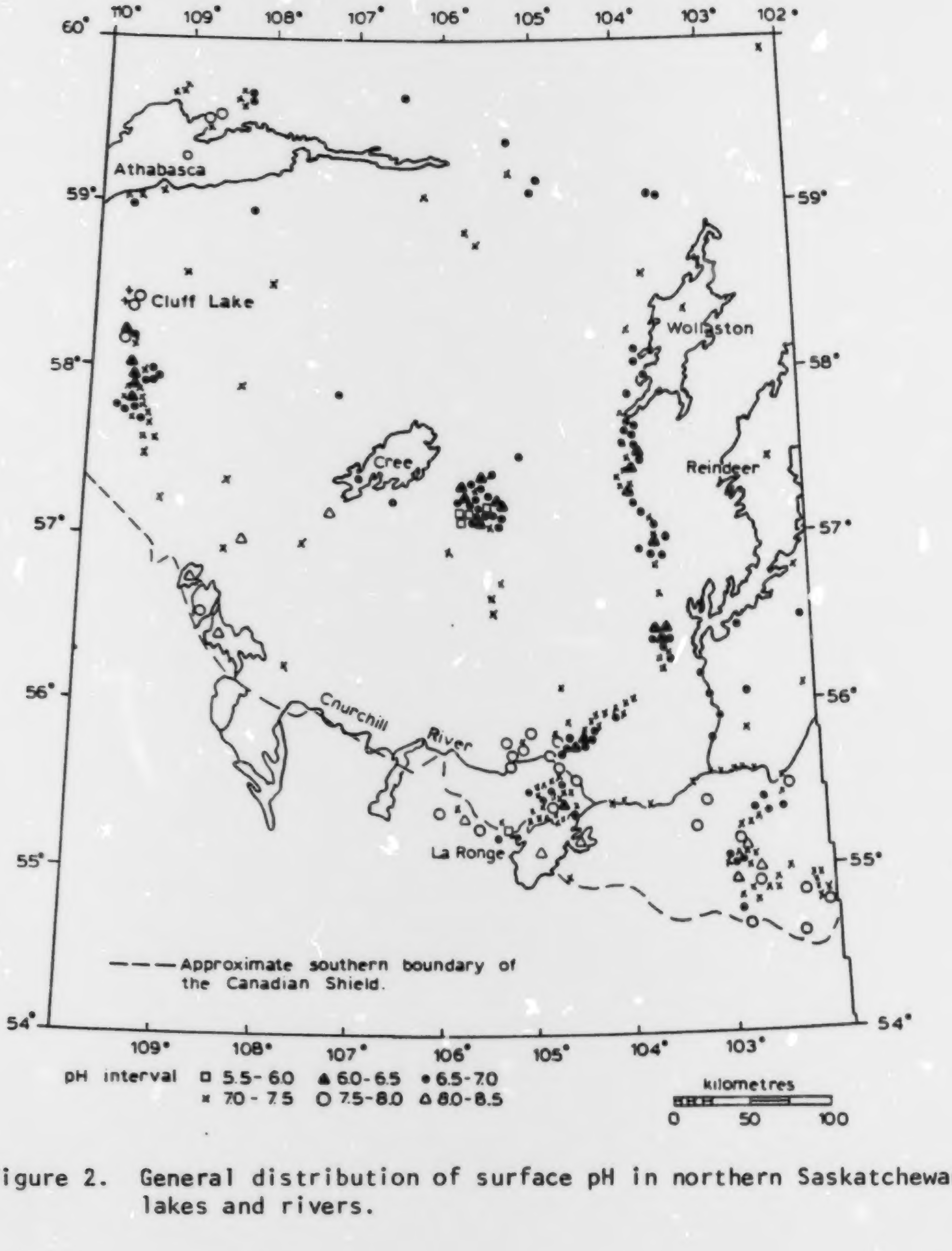

110°
109°
108°
107°
106°
105°
104°
103°
102°
kilometres
0
50
100
Alkalinity intervals as mg/L $CaCO_3$
■ 0 - 10
∘ 10 - 20
△ 20 - 40
x > 40
59°
58°
57°
56°
55°
54°
53°
Athabasca
Cluff Lake
Wollaston
Cree
Reindeer
Fort McMurray
Churchill River
La Ronge
Cold Lake
FlinFlon

Figure 1. General distribution of surface total alkalinity in northern Saskatchewan lakes and rivers. Broken line indicates the approximate southern boundary of the Canadian Shield. Lakes north of heavy solid line are considered highly sensitive to acidification.


110°
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54°
Athabasca
Cluff Lake
Wollaston
Cree
Reindeer
Churchill
River
La Ronge
Approximate southern boundary of the Canadian Shield.
pH interval □ 5.5-6.0 ▲ 6.0-6.5 ● 6.5-7.0
× 7.0-7.5 ○ 7.5-8.0 △ 8.0-8.5
kilometres
0
50
100

Figure 2. General distribution of surface pH in northern Saskatchewan lakes and rivers.

3.3 CALCIUM

Calcium concentrations of 303 waters in the study area ranged from 0.33 to 31.60 mg/L with a mean of 5.71 mg/L ± 5.34 mg/L (one standard deviation). About 54% of the waters measured had Ca of 4 mg/L or less, 25% had 4 to 8 mg/L, and 21% had more than 8 mg/L (Figure 3).

3.4 MAGNESIUM

Measurements of Mg are available for 302 lakes and rivers in the Shield and fringe Shield areas. They varied from virtually 0 to 10.7 mg/L with an average of 1.99 mg/L and a standard deviation of 1.75 mg/L. Sixty-five percent of the waters surveyed had Mg of 2 mg/L or less, 16% had 2 to 3 mg/L, and 19% had more than 3 mg/L (Figure 3).

3.5 EMPIRICAL RELATIONSHIPS

The following relationships derived from observed data are important for the assessment of the state and rate of acidification in lakes.

3.5.1 Alkalinity vs Calcium and Magnesium

Concentrations of alkalinity in Saskatchewan's Shield and fringe Shield lakes were found to be highly correlated to concentrations of Ca. The least-squares linear regression for this relationship is:

$$\text{Alkalinity } (\mu\text{eq/L}) = 22.24 + 1.28\,(\text{Ca}) \quad (r = 0.93;\ n = 282)$$

However, for the same lakes, the sum of Ca and Mg is a better indication of alkalinity than Ca alone. As indicated in Figure 4, the sum of Ca and Mg is very close to the alkalinity on an equivalent weight basis. This means that concentrations of alkalinity can be estimated from measurements of Ca and Mg when direct measurements of the former are not available.

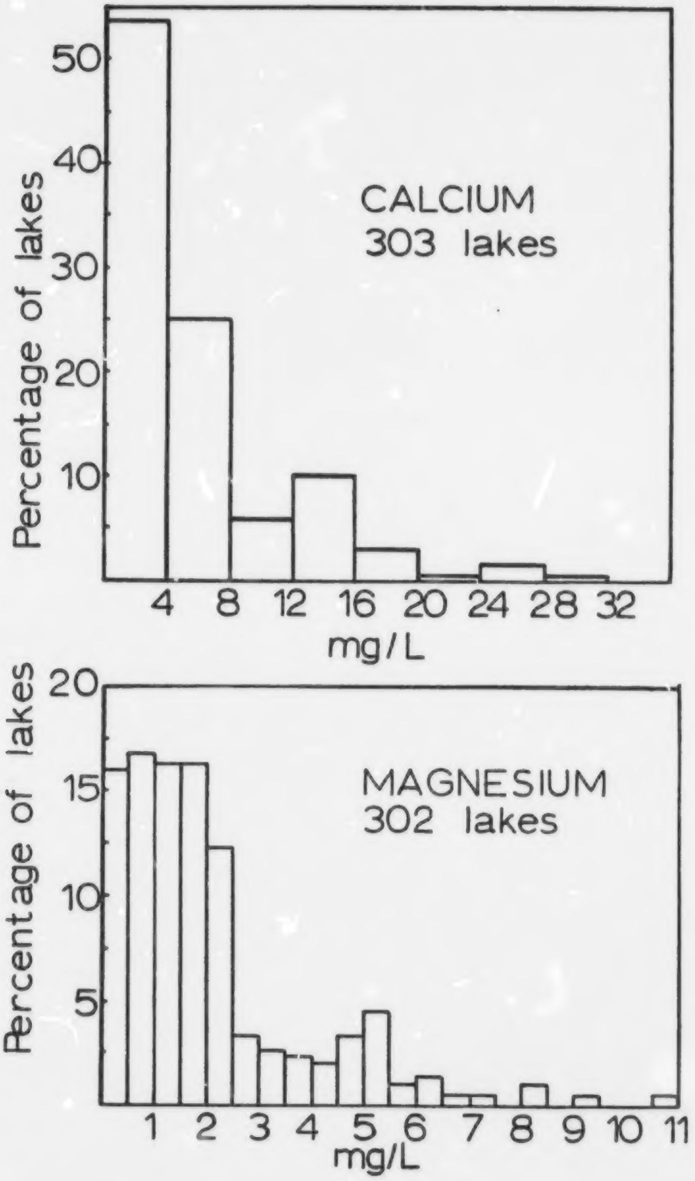

Figure 3. Distribution of Ca and Mg concentrations in northern Saskatchewan lakes.

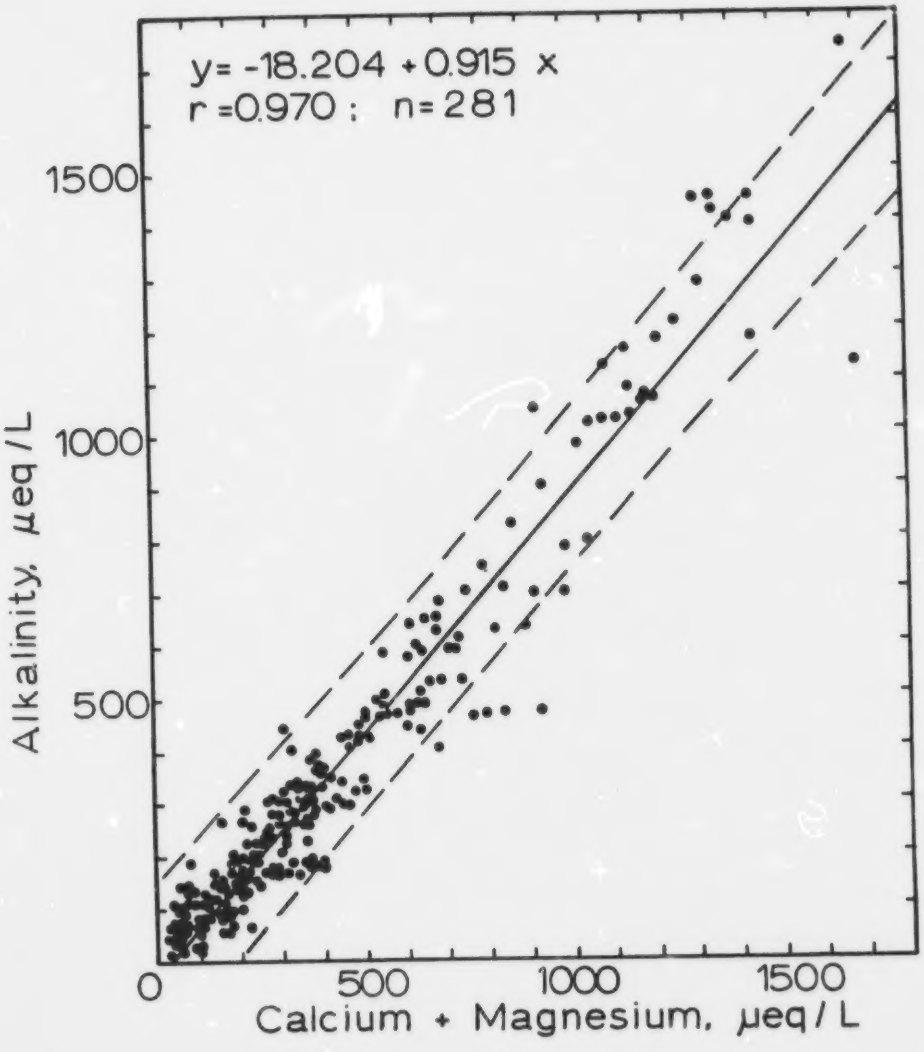

Figure 4. Relationship between alkalinity and Ca + Mg for northern Saskatchewan lakes. Broken lines indicate 95% confidence limits of predicted values.

3.5.2 Alkalinity and Acid Consumption

The ability of a water to consume or neutralize acids varies with the amount of its alkalinity. This relationship was empirically determined for Saskatchewan's Shield and fringe Shield lakes to a pH of 5.5, based on 278 potentiometric titrations with a standard acid solution (Figure 5). Other pH levels, for example 6.0, could be selected, but pH 5.5 appears to be of some chemical significance.

A comparison of the regression line with the 1:1 line indicates that for this group of lakes, at pH 5.5, the amount of alkalinity in the water is nearly exhausted. A closer examination of the distribution of data points around the regression reveals that for lakes with lower buffering capacity, the alkalinity is generally exhausted before pH 5.5 is reached. On the other hand, for lakes with higher buffering capacity, there is still some alkalinity left even when the pH falls below 5.5. Apparently, for this group of Saskatchewan lakes, pH 5.5 represents a critical point in the event of acidification; when this pH level is approached, drastic changes in pH will occur with a small amount of acid input. This pH is very close to the inflection point in an acid-base titration curve (Figure 6).

3.5.3 Surface Area and Mean Depth of the Lakes

Data of both surface area and mean depth are available for 143 lakes from the Shield and fringe Shield regions in northern Saskatchewan. These lakes varied from very small (<0.1 km^2) to very large (up to 7 900 km^2) in surface area. Mean depth of these lakes ranged from 1.1 to 30.5 m with the majority of them being 9 m or less (Figure 7). In general, mean depth increases with increasing surface area, but the range of variation in mean depth for a given surface area is very large (Figure 8). Thus, the relationship between mean depth and surface area presented here can only be used to obtain a first approximation of mean depth from area measurements. While this kind of approximation is needed in view of the lack of depth soundings for most Saskatchewan lakes, it cannot be taken as a substitute for direct sounding.

Mean depth, an indication of the volume of a lake, and the acid consumption of the lakes, form the basis of the nomograph

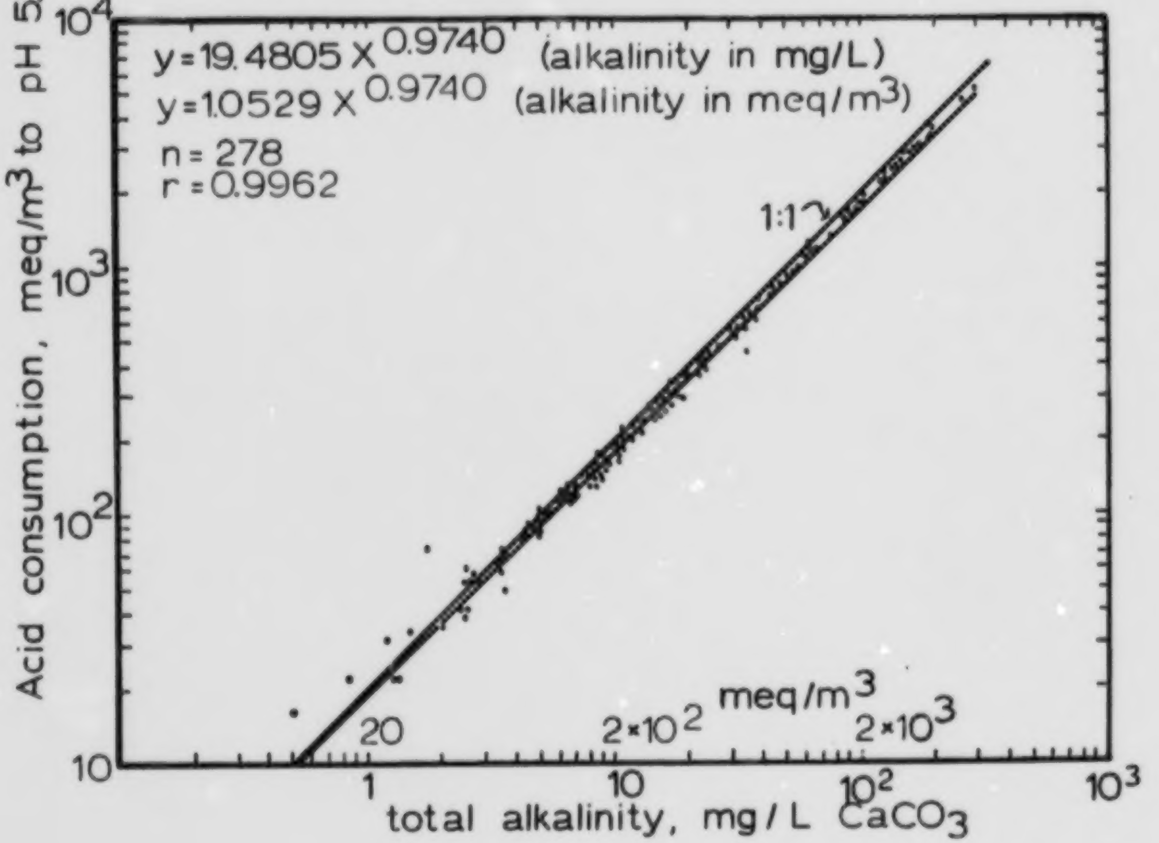

Figure 5. Acid consumption of lake waters in northern Saskatchewan.

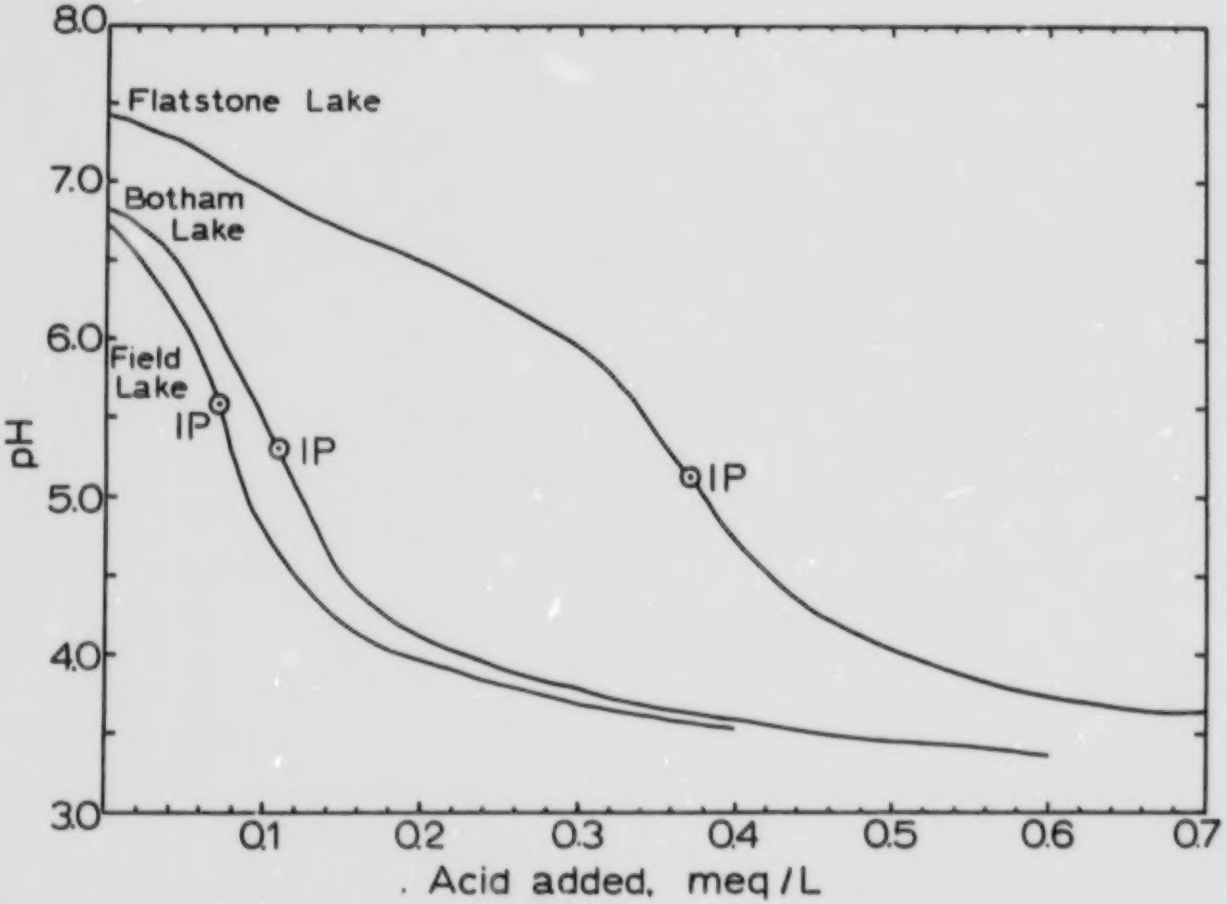

Figure 6. Potentiometric titration curves for these three shield lakes in northern Saskatchewan illustrating point of inflection in the curve (marked ⊙ IP)

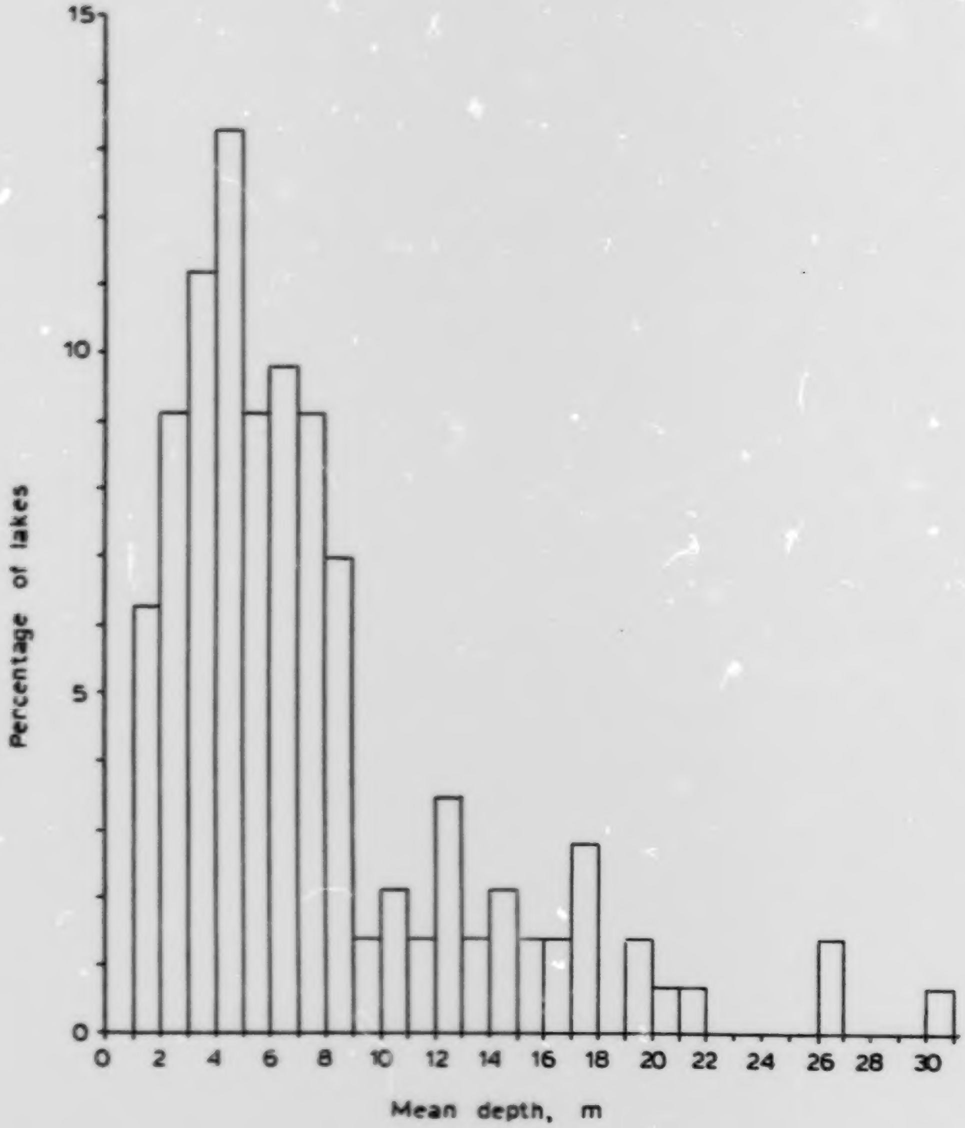

Figure 7. Histogram of mean depth (m) of 143 northern Saskatchewan (Canadian Shield) lakes.

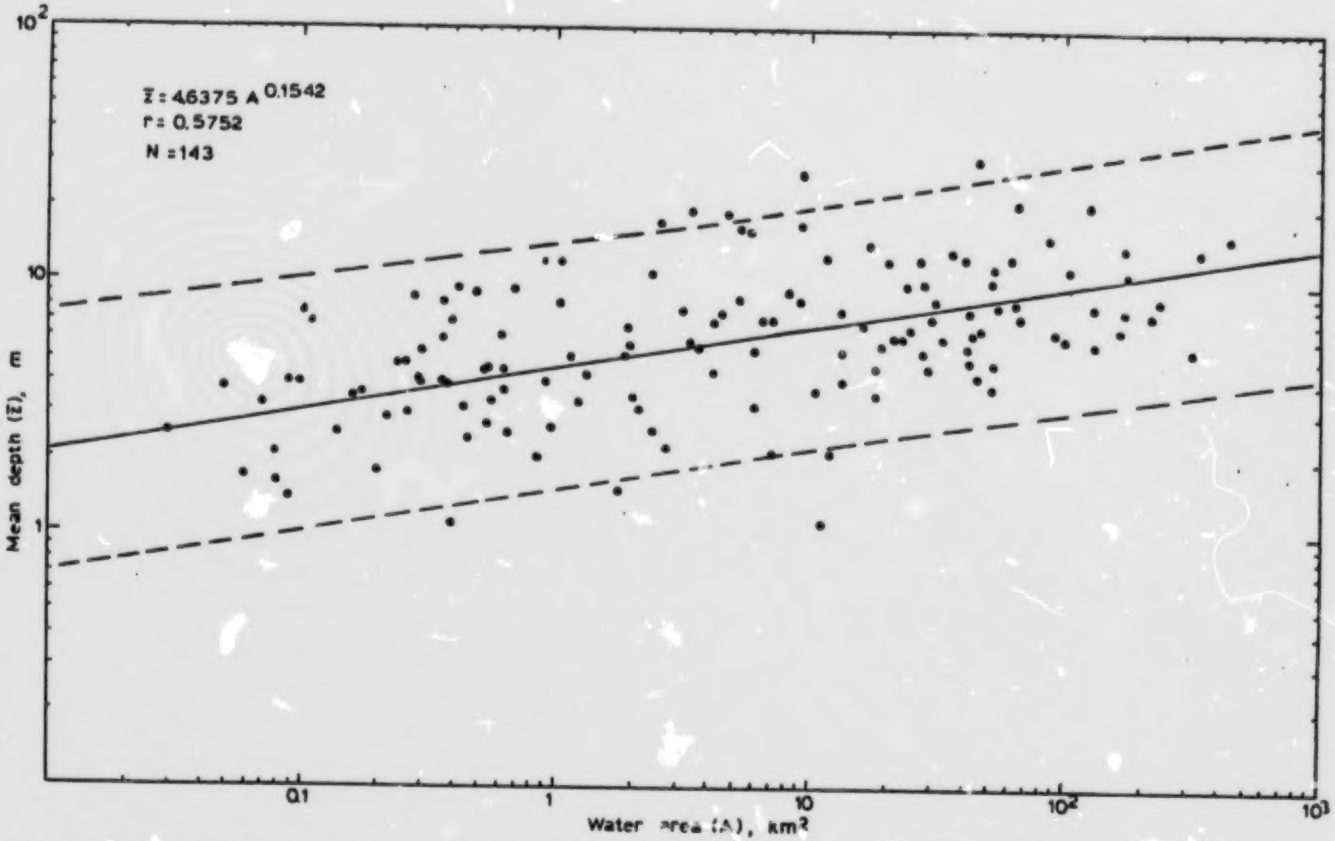

Figure 8. Relationship between water area and mean depth for 143 northern Saskatchewan (Canadian Shield) lakes. Broken lines indicate 95% confidence limits of predicted values. Four lakes with area greater than 1000 km^2 (1155 - 7900 km^2) not shown.

depicting the rate of acidification that may be expected under certain sulphur deposition rates (Figure 9).

4. DISCUSSION

On the average, the concentrations of alkalinity, Ca abnd Mg of waters from the Shield and fringe Shield regions in northern Saskatchewan are much lower than the world average, but are within the range found in Shield regions elsewhere in North America and Scandinavia (Figure 10). Further, the relationship found between the alkalinity and the sum of Ca and Mg for Saskatchewan's Shield and fringe Shield lakes (Figure 4) is also very similar to that for other Shield lakes in the world (Henriksen 1980). Compared with lakes in the Greater Sudbury area (Conroy et al. 1978), Saskatchewan Shield lakes have higher average alkalinity (17.9 mg/L vs 9.0 mg/L), but the average concentrations and ranges of Ca and Mg for these two groups of lakes are about the same. The pH of the 209 Sudbury lakes that were surveyed ranged from 4.3 to 8.4, 80% of which were below 7.0, 18% of the lakes were considered acidified (pH < 5.5). In comparison, the pH of the 305 Saskatchewan lakes varied from 5.56 to 8.20; only 39% of them had pH less than 7.0 and none were below pH 5.5.

Thus, the lower average alkalinity and pH for the Sudbury lakes are likely the result of acidification over the past three decades or so. By comparing present-day measurements with limited historical pH data, the rates of acidification have been estimated. They were between 0.09 and 0.16 pH units/yr for the lakes in the Sudbury area (Conroy et al. 1978, Beamish and Harvey 1972) and from 0.03 to 0.05 pH units/yr for lakes in Scandinavia (Gjessing et al. 1976).

Most of the known acidified lakes are located in areas of resistant granitic and siliceous bedrock with thin and patchy soils, which can apparently provide very little buffering to the waters. The watershed on the Shield in northern Saskatchewan falls into this category as is reflected in the chemistry of its waters. Therefore, there is reason to believe that in the event of acid rain, many of the Saskatchewan Shield lakes may be affected to the same extent and within a similar time frame as those in southern Ontario.

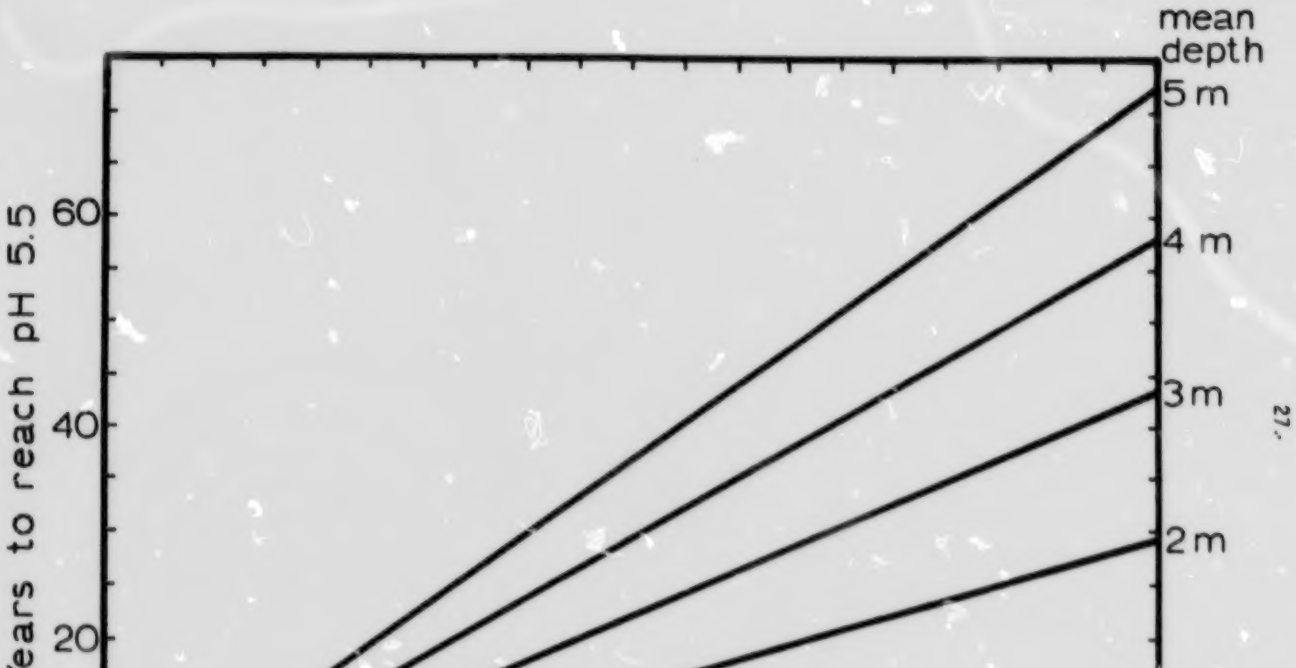

Figure 9. Nomograph depicting expected rate of acidification to pH 5.5 under various buffer capacities and a given S-deposition rate of 0.4 g/m^2/yr.

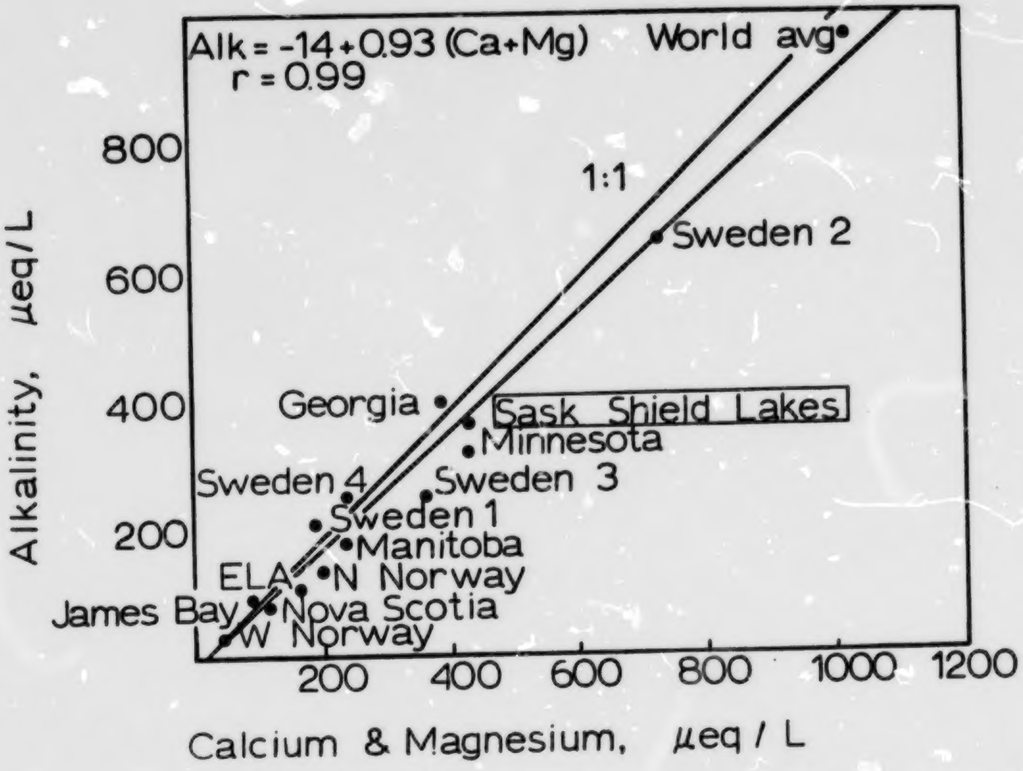

Figure 10. Relationship between alkalinity and the sum of the non-marine calcium and magnesium. (Henriksen 1980).

The primary buffering of an aquatic system is provided by the bicarbonate content. Alkalinity is commonly used to indicate the bicarbonate buffering capacity. Calcium alone or together with Mg can also be a good indicator of buffering capacity, as their concentrations are closely related to that of alkalinity for the Shield lakes (Figure 4). The United States-Canada Research Consultation Group (Altshuller and McBean 1979) has proposed a set of criteria to assess the sensitivity of lakes to acidification. The criteria based on contents of alkalinity and Ca are as follows:

Sensitivity	Alkalinity (mg/L CaCO$_3$)	Ca (mg/L)
Highly sensitive	0 to 10	0 to 4
Moderately sensitive	10 to 20	4 to 8
Least sensitive	>20	< 8

According to the above guidelines, 44% of the lakes studied, mostly located in the northern part of the Shield, may be considered as highly sensitive to potential acid rain. To be more specific, this part of the Shield encompasses the area north of a curve connecting the Churchill River at the Saskatchewan-Manitoba border, the southwest end of Cree Lake and Lake Athabasca at the Alberta border. This curve is roughly parallel to the southern Shield boundary (Figure 1). Included in this region are the drainage systems of Athabasca, Cree, Wollaston, and Reindeer lakes. However, Lake Athabasca and the area north of it must be excluded from the region, because lakes in this area are moderately to least sensitive to acidification according to their buffering capacity.

South of the above very sensitive zone, there exists a great deal of variation in buffering capacity from lake to lake, apparently due to local differences in carbonate mineral deposits and soil depth. This zone, usually considered as Shield boundary or fringe Shield region, consists of the Churchill River and its immediate watershed north and south (Figure 1). Based on the contents of alkalinity and Ca, lakes in this zone are generally moderately to rather insensitive to acidification. However, many highly sensitive lakes can also be found in this zone. These are usually small lakes draining a limited watershed area covered with thin glacial deposits.

The results of this study show that there are lakes in northern Saskatchewan which already have low alkalinities and pH (<6.6). These are likely natural conditions rather than the result of acid rain associated with anthropogenic sources. Based on limited measurements of precipitation chemistry at the Cree Lake Station of the Canadian Network for Sampling Precipitation (CANSAP) wet deposition rates of $S-SO_4$ and $N-NO_3$ in 1978 were 1.8 and 0.5 kg/ha/yr, respectively. The pH in rain at the same station during the same year ranged from 4.8 to 5.8. The above wet deposition rates of sulphate and nitrate can still be considered at or near global background levels. The rain at Cree Lake does show some acidification at present (the pH of clean rain is 5.6), but the acidity is considered definitely due to the lack of buffering capacity in the rain, rather than to an anthropogenic source of emission (Shewchuk 1981). Thus, it would appear that the low alkalinities and pH in some northern Saskatchewan lakes are just a reflection of the geochemical and soil conditions of their watersheds. If a lake and its watershed contain very little buffering capacity, even clean rain, which is already mildly acidic, can in a long term gradually consume some of the alkalinities and reduce the pH of the water.

The question of whether or not some of the northern Saskatchewan lakes are being affected by acid rain can be evaluated further by plotting concentrations of Ca and pH. In studying lake acidification problems in Norway, Henriksen (1979) developed an empirical curve for Ca and pH which can be used to evaluate the status of lakes with respect to acidification. He found that lakes lying in areas receiving highly acidic precipitation ($pH < 4.6$) could be separated by the curve from those lying in areas not receiving acid rain. A plot of Ca and pH from Saskatchewan's Shield lakes in relation to Henriksen's curve (Figure 11) indicates that none of these Saskatchewan lakes are being affected by acid rain. Those lakes, which lie above the curve, happen to be small muskeg lakes. The loss of alkalinity in these lakes is likely due to the presence of large amounts of Sphagnum moss in the immediate drainage area.

Knowing that surface waters in northern Saskatchewan are sensitive to potential acid rain is not enough, because sensitivity is

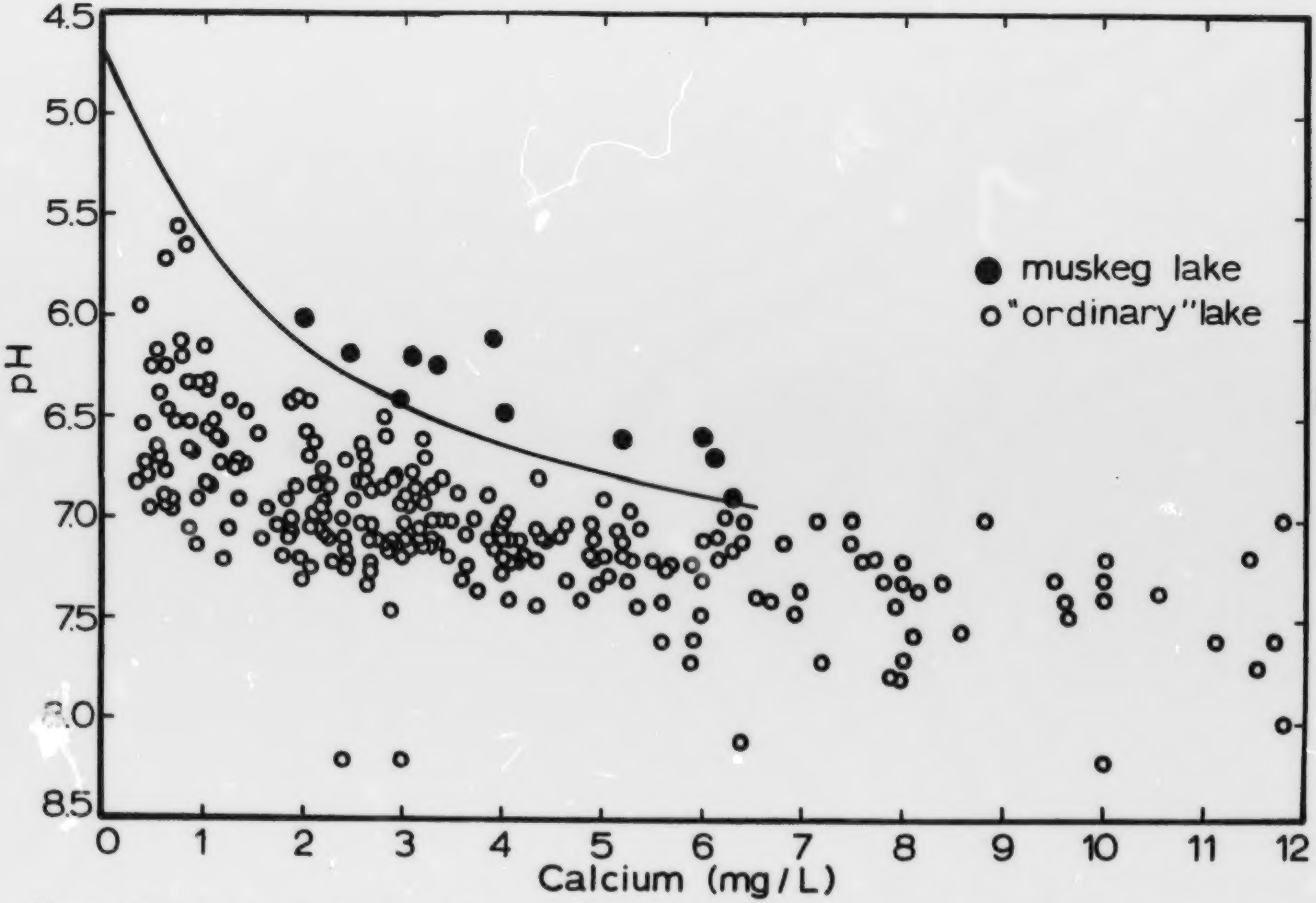

Figure 11. Relationship of calcium and pH in Saskatchewan's Shield lakes to empirical curve of Henriksen.

a relative term which does not indicate rates of response of these lakes to acidification. The rate of acidification of a lake depends on the buffering capacity of not only the water, but also its watershed. The buffering capacity, in turn, is determined by a number of factors including the geochemistry, geomorphology, and hydrology of the whole land-water system. Until a quantitative knowledge of how these factors interact to control the buffering capacity of the system is developed, it will be difficult to assess accurately the rate of acidification in lakes (National Research Council Canada 1981).

In spite of the lack of a comprehensive understanding of the buffering capacity of the watershed and its waters, some idea of the rate of acidification in lakes can, nevertheless, be obtained by simply comparing historic with present-day pH levels of acidified lakes. Unfortunately, reliable long-term historic data are too scarce to provide good trends of lake acidification.

Alternatively, ideas regarding the rate of acidification may come from a spatial comparison of present-day data which are far more extensive than historic measurements. For example, Henriksen (1980) has developed a nomograph to predict the pH of lakes on the basis of the relationship between Ca or Ca + Mg and the weighted average (H^+) in precipitation or non-marine SO_4 concentrations in lake water. This model can be used to predict the rate of acidification in lakes if a time trend can be assigned to pH changes in precipitation. The nomograph of Henriksen was modified slightly and redrawn here (Figure 12). The position of some northern Saskatchewan lakes with low buffering capacity are shown as a group in the nomograph, based on SO_4 concentrations of the lakes and precipitation pH at Cree Lake.[1] However, until future changes in precipitation pH due to increased emissions of SO_2 and NO_x can be predicted, it is difficult to use this model to estimate the rate of acidification in Saskatchewan lakes.

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[1] Measurements of SO content are available for 122 lakes in the Shield region; nearly all of them are less than 2 mg/L (42 µeq/L). The precipitation pH at Cree Lake ranged from 4.6 to 6.3 between May 1977 and June 1979 (CANSAP data).

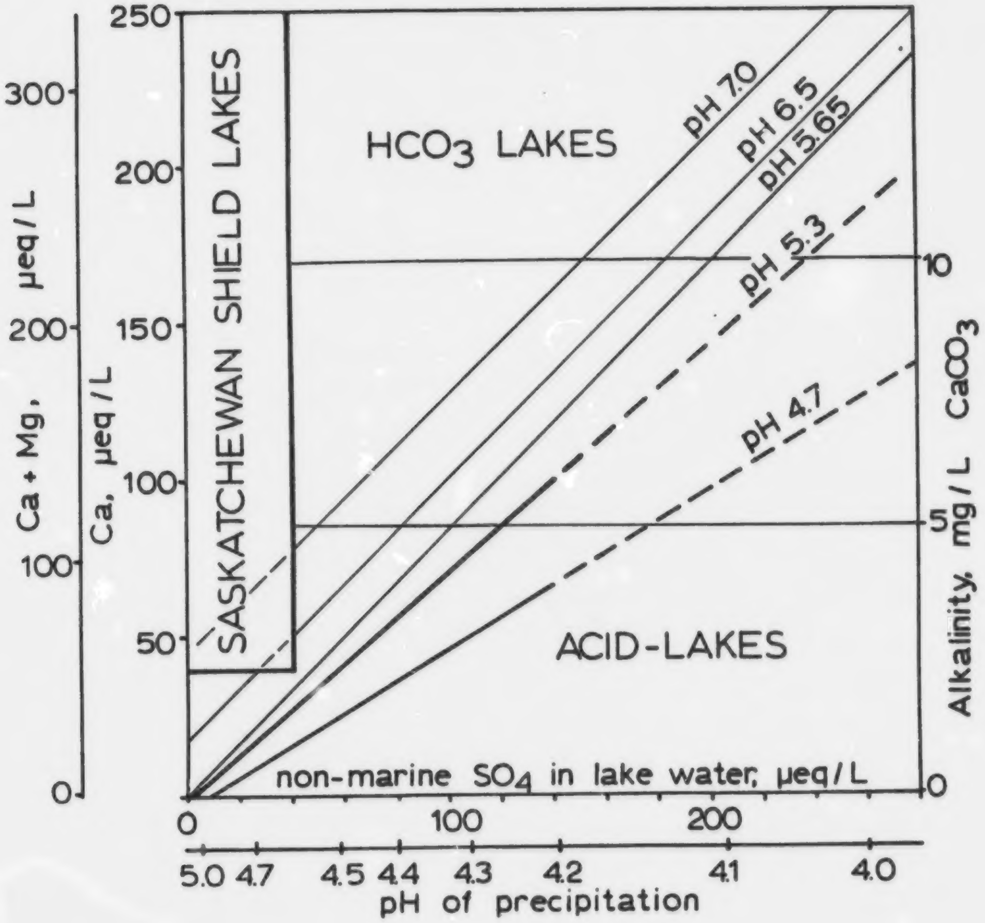

Figure 12. Position of Saskatchewan Shield lakes in Henriksen's nomograph for predicting the pH of lakes at given weighted-average H+ in precipitation. Lines for pH 5.65, 6.5, and 7.0 are theoretical.

Furthermore, it is noted that in Henriksen's model, no consideration is given to the effect of mean depth or volume of the lakes. Clearly, other factors being equal, the amount of acid input a lake can neutralize is proportional to its mean depth. Consequently, even if the temporal changes in precipitation pH can be predicted, there will still be considerable uncertainty in applying Henriksen's model to northern Saskatchewan where there is a great deal of variation in mean depth from lake to lake. It is, therefore, necessary to consider a different approach using the same basic assumption that the lake acidification process is like a large scale acid-base titration, but taking into consideration the mean depth of the lake. For lakes situated in very resistant Shield terrain, this assumption is apparently valid, at least until the pH of the lake water falls to about 5.3 (Henriksen 1980). Thus, from laboratory titration of water samples, the amount of acid consumed by lake water can be calculated to a certain pH endpoint (e.g., 5.5) with respect to the alkalinities of the lakes (Figure 5). Further, by knowing or assuming the rate of acidic deposition (e.g., 0.4 g $S/m^2/yr$, or 25 meq $acidity/m^2/yr$) a nomograph can be constructed to predict the rate of acidification to a predetermined pH level (e.g., 5.5), given the mean depth and the alkalinity of the lake (Figure 9). For example, from the nomograph, a northern Saskatchewan lake having a mean depth of 5 m and an original alkalinity of 5 mg/L may be expected to acidified to pH 5.5 within about 20 yrs if the average annual acidic deposition is 25 meq/m^2. On the other hand, another lake of the same mean depth, but having twice as much buffering capacity, will take twice as long (40 yr) to be acidified to the same pH level. Only one acidic deposition rate is considered in the nomograph. However, other rates can easily be used. For example, with an acidic deposition rate of 50 $meq/m^2/yr$, it will only take 10 yrs for a lake of 5 m mean depth and 5 mg/L alkalinity to be acidified to the critical pH condition.

The nomograph indicates that in the event of acid rain, those shallow and poorly-buffered Shield lakes in northern Saskatchewan may be acidified to critical conditions within two to three decades. However, as mentioned earlier, several factors may be involved in determining the rate of acidification in lakes. Therefore, the rates predicted from the nomograph must be viewed with caution. The prediction is only intended to provide a crude first approximation. It can undoubtedly be improved if more about the various factors affecting the buffering capacity is known.

5. CONCLUSIONS

The present study has identified and described the elementary features and regional distribution of aquatic habitat vulnerable to acidification in Saskatchewan. The area north of a line from Lake Athabasca at the Alberta boundary to the southwest of Cree Lake and the Churchill River at the Manitoba boundary (Figure 1) is considered highly sensitive. Shallow (mean depth < 5 m) and poorly-buffered (alkalinity <5 mg/L) lakes are particularly vulnerable.

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SESSION IV

HEALTH

AN OVERVIEW OF THE EFFECTS OF ACID FORMING GASES ON HUMAN HEALTH

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ABSTRACT

(An abstract was not submitted)

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1. INTRODUCTION

This presentation is intended as a general overview of the health effects of acid forming gases. The known effects of the three acid forming gases of greatest importance in Alberta, sulphur oxides (SO_x), nitrogen oxides (NO_x), and hydrogen sulphide (H_2S), will be briefly reviewed. This will be followed by a brief discussion on health effects of acid rain. In conclusion, some thoughts on future directions for research and priorities for action will be presented.

2. ACID FORMING GASES

2.1 SULPHUR DIOXIDE

Sulphur dioxide is a soluble, colourless gas arising from the combustion of sulphur present in coal and from the bisulphite digestion of pulp in pulp and paper mills. It is also used in bleaching of textiles and other industrial processes. Sulphur dioxide is a very irritating substance and therefore has good warning properties. Most people are able to tolerate up to 5 parts per million (ppm) without difficulty, and can be acclimatized to higher levels. Exposure to higher concentrations results in asphyxia or chemical bronco-pneumonia. In Alberta, the 8-hour occupational exposure limit (OEL) for sulphur dioxide is 2 ppm, while the 15-minute OEL is 5 ppm. Environmental standards are less than one tenth of the OEL, ranging from 0.2 ppm for 1/2 hour to 0.01 ppm as an annual arithmetic mean (Table 1). The environmental standards are much lower than the occupational standards, of course, because exposure to air pollution is 24 hours per day rather 8 hours or 12 hours at a time. As well the population contains hypersusceptible people such as children, asthmatics and old people (Table 2) who cannot be screened out or screen themselves out of exposure to air pollution as they could to exposure in the workplace.

In recommending or establishing environmental standards, scientists and regulators have relied on two main sources of data, inhalation toxicology studies on humans and animals and epidemiological studies in human populations. Many of these studies are cited and analyzed in the excellent criteria document from the

Table 1. Alberta air quality standards.

CONTAMINANT	ALBERTA STANDARDS
Sulphur Dioxide	
Annual arithmetic mean	0.01 (30)
24-hour average	0.06 (170)
1-hour average	0.17 (485)
0.5-hour average	0.20 (570)
Occupational exposure limit (8 hr.)	2.00 (5 700)
Short-term occupational exposure limit (15 min.)	5.00 (14 300)
Hydrogen Sulphide	
24-hour average	0.003 (4)
1-hour average	0.010 (14)
0.5-hour average	0.012 (17)
Occupational exposure limit (8 hr.)	10.000 (14 000)
Short-term occupational exposure limit (15 min.)	15.000 (21 000)
Nitrogen Dioxide	
Annual arithmetic mean	0.03 (60)
24-hour average	0.10 (200)
1-hour average	0.20 (400)
Occupational exposure limit (8 hr.)	5.00 (9 000)

Table 2. Populations with higher the average risk for health effects of air pollutions.

Pre-existing Pulmonary Disease

- Asthma
- Chronic Bronchitis
- Cystic Fibrosis
- Emphysema

Pre-existing Cardiac Disease

- Congestive heart failure
- Coronary insufficiency
- Cor pulmonale
- Hypertensive heart diseasee
- Rheumatic heart disease

Exposure to additional Environmental Factors

- Cigarette smoking
- Occupational exposures (dusts, fumes, gases, etc.)

Other Factors

- Age (infants, preschool children, elderly)
- Social factors (low income, malnutrition, overcrowding, etc.)

World Health Organization (1979) on sulphur oxides. On the basis of these studies, the World Health Organization has estimated a number of health effect thresholds, which are documented in Table 3. It is on this type of analysis that standard setting is based.

The figures presented in Table 3 may appear to be very solid and precise. In reality, however, the assessment of risk when dealing with biological populations is much more of an art than a science, and such estimates may be out of an order of magnitude or more. Reasons for this include:

1. Both toxicological and epidemiological research is based on assumptions that may not be correct (e.g., that the analytical equipment used measures the levels of airborne contaminants correctly). Much criticism has been directed at the community health environmental surveillance system (Colucci 1977)(C.H.E.S.S.) on the grounds that the analytical techniques used were not adequate.
2. There are a multitude of other confounding factors, particularly with epidemiological studies, such as smoking, climatic factors in the different regions studied, co-existing occupational exposures, etc. For example, in a large New York study (Buckley et al. 1973), a number of factors were correlated with daily mortality rates. Factors which came ahead of air pollution in explaining the variance in mortality rates included season of the year, extreme high temperatures, influenza episodes, sudden temperature shifts, holidays (Christmas and New Years being highest) and day of the week (Monday being high, Wednesday and Thursday 3% lower than Monday).
3. The methodology used in inhalation toxicology studies and epidemiological studies makes the results of the analysis difficult to apply. Inhalation toxicology studies generally look at one gas rather than many interacting ones, which is the usual situation in the

Table 3. Summary of reported effects of inhalation of sulphur dioxide.

Concentration (ppm)	Effects or comments
0.035	W.H.O. estimated threshold for respiratory effects from long-term exposure (increased respiratory symptoms in adults and children above this level)
0.08	W.H.O. estimated threshold for worsening the condition of patients with existing respiratory disease from short-term exposure (e.g. increased asthma attack rate, increased illness score among bronchitis)
0.18	W.H.O. estimated threshold for excess mortality among the elderly or chronically sick from short-term exposure
0.35	Mortality rate three times normal in epidemiological study, London, England
0.3 - 1.00	Detectable by taste
0.75 - 1.00	Lowest level causing detectable decrease in FEV, FVC, and MMFR in human lab studies (2 hour exposure)
8 - 12	Immediate irritation to throat
20 - 50	Immediate irritation to eyes, nose and throat, inducing sneezing, rhinorrhea, and cough

> atmospheric environment, while epidemiological studies often draw conclusions about one substance while the population studied is exposed to a variety of gases. As Goldsmith (1976) put it, "the epidemiologists are always looking at too much and drawing inconclusive results, while the experimentalists are looking for too little and are drawing conclusive results".

With respect to air pollution generally, because of the factors that I have mentioned and others that I haven't, Goldsmith (1976) concluded that as many as 10% or as few as 0.1% of health problems could be related to air pollution, a thousand-fold difference.

2.2 NITROGEN OXIDES

Nitric oxide, which is relatively inert biologically, is produced by high pressure combustion (e.g., in gasoline engines) by the oxidation of atmospheric nitrogen. Nitric oxide is slowly oxidized in air, more rapidly in the presence of photochemically activitated hydrocarbons, to nitrogen dioxide. Nitrogen dioxide occurs in two forms, NO_2 (red) and N_2O_4 (colourless). Nitrogen oxides may also be produced by the combustion of materials rich in nitrogen (e.g., nitrocellulose in x-ray film or tri-nitro-toluene in mines) or by the fermentation of silage, which contains nitrates used in fertilizers. The gas particularly dangerous as it is not very irritating and therefore has poor warning qualities (unlike sulphur dioxide) and is not very soluble, so it penetrates deeply into the lungs. High doses, which are encountered in occupational settings, lead to pulmonary edema. This may subside after a few hours if the patient survives, but respiratory symptoms recur a week or two weeks later, a reaction medically known as bronchiolitis obliterans. Resolution of the second phase is gradual, and can leave the patient with permanent scarring of the lungs. The exposure level required to produce pulmonary edema (more than 100 ppm; see Table 4) is never seen in association with community air pollution. Even urban

Table 4. Summary of reported effects of inhalation of nitrogen dioxide.

Concentration (ppm)	Effects or comments
0.05 - 0.075	No effect on prevalence of chronic respiratory symptoms
0.08 - 0.15	Increased respiratory disease in children
0.11 - 0.42	Odour threshold
0.50	W.H.O. estimated threshold for respiratory effects of short-term exposure
0.7-5	Increased airways resistance in laboratory studies after 10 mins. to 2 hrs. exposure
10 - 20	No discomfort
100 - 150	Delayed pulmonary edema after 30 to 60 minutes exposure
200 - 700	Fatal pulmonary edema after less that one minute exposure
More than 1 700	Lethal in minutes

concentrations, which are highest because of the number of internal combustion engines in operation, are on the average less than 0.1 ppm and rarely reach 0.5 ppm even for very brief periods in the most polluted cities. In both human and animal inhalation toxicology studies, the lowest concentration of NO_2 that has been found to adversely affect pulmonary function with short-term exposure is approximately 0.7 ppm. At lower doses, there may be some impairment of the lung's ability to deal with biological pathogens, resulting n increased susceptibility to respiratory tract infections.

In its criteria document on the oxides of nitrogen, the World Health Organization (1977) estimated 0.5 ppm as the threshold for health effects from short-term exposure. The World Health Organization task group was unable to come to any conclusive threshold for long-term exposure to NO_x. Epidemiological studies have been carried out in this area, but have been generally complicated by simultaneous exposures to several other air pollutants such as SO_x, particulates and photochemical oxidants. The 8-hour occupational exposure limit for nitrogen dioxide in Alberta is 5 ppm. The environmental standards range from 0.20 parts per mean for 1 hour, 0.10 parts per mean for 24 hours and 0.03 parts per mean as an annual arithmetic mean (Table 5).

2.3 HYDROGEN SULPHIDE

Hydrogen sulphide is a soluble gas with both local irritant and systematic toxic effects (7). It is produced by decaying organic matter (e.g., in sewers) and is also found in tanneries and, of course, the petroleum industry. Death from acute exposure is a result of depression of the respiratory centre (Table 6). If the victim is revived, there are generally no systemic sequelae. Lower doses are irritating to the lungs and produce pulmonary edema, similar to the effect of sulphur dioxide. The eyes are also affected. The conjunctivitis which results from exposure is commonly referred to in the sour gas industry as "gas eye". Finally, there is paralysis of the olfactory system. This is almost instantaneous at high concentrations and may lead to a false sense of security among persons exposed to high levels of H_2S.

Table 5. Alberta air quality standards - Nitrogen Dioxide

Contaminant	Alberta Standards ppm	($\mu g/m^3$)
Annual arithmetic mean	0.03	(60)
24-hour average	0.10	(200)
1-hour average	0.20	(400)
Occupational exposure limit (8 hour)	5.00	(9 000)

Table 6. Concentrations of H_2S and Human Health Effects

Concentration (ppm)	Classification	Effects
0.3	Odour Threshold	Odour apparent
10	Threshold Limit Value	None
20 - 50	Irritation - minimal	Minimal eye and lung irritation. May have digestive upsets.
50 - 150	Irritation	Olfactory nerve paralysis can occur at 150 ppm.
150 - 300	Irritation - severe	Loss of smell in ± 30 min. Severe eye irritation. Severe lung irritation
300 - 500	Dangerous	Loss of smell in ± 30 min. Severe eye irritation. Severe lung irritation with pulmonary edema after 30 min. exposure.
500 - 700	Life Threating	Systemic symptoms within one hour. Headache, dizziness; unconsciousness and death within 4-8 hours. Serious irritation to respiratory tract and eyes (conjuctiva and epithelium) within 30 mins. Coughing, bronchitis pharyngitis, dyspnea, possible pulmonary edema, photophobia, conjunctivitis and keratitis.

Continued ...

Table 6. Concluded.

Concentration (ppm)	Classification	Effects
700 - 1 000	Life Threatening	Systemic effects predominate over local irritant effects. Systemic symptoms within 30 mins. Collapse, asphyxia, death within one hour.
100 - 2 000	Life Threatening	Systemic effects predominate over local irritant effects. Immediate systemic symptoms. Stimulation of respiration (hyperpnea), followed by respiratory inactivity (apnea), collapse, asphyxia, and death within 30 minutes.
+2 000	Lethal	Systemic effects predominate over local irritant effects. Paralysis of respiratory center, immediate death.

From Greenhill, S. Human health effects of hydrogen sulphide. Alberta Environment. 1978. pp. 11-12.

As opposed to NO_x and SO_x, community air pollution with H_2S is an episodic event. There has been one major disaster reported in the medical literature. This was in Poza Rica, Mexico where, in November 1950, the sudden release of a large quantity of H_2S from a refinery in the presence of weak winds and a low inversion caused illness in 320 persons living adjacent to the plant boundary, and death in 22 persons of all ages (8). There is little in the way of either experimental or epidemiological research on the effects of low doses of hydrogen sulphide.

The 8-hour occupational exposure limit in Alberta is set at 10 ppm (Table 7), while the environmental standards are much more conservative, ranging from 0.012 ppm as a half hour average to 0.003 ppm as a 24-hour average.

2.4 SUMMARY

The evidence presented above and the current medical literature suggests that acid forming gases deserve less priority than they have been givn in the past as a means of preventing acute or chronic health problems in exposed human populations. Programs to prevent cigarette smoking, occupational exposures and indoor air pollution would have proportionately far greater influences on the prevention of human health effects from acid forming gases in the outdoor air.

This does not mean to say that air pollution is not important, but that the effects of air pollution and the measures necessary to control it should be judged on their general impact on the environment (i.e., effects on lakes, forests, wildlife, and livestock) rather than on direct human deaths.

3. "ACID RAIN"

So_x, NO_x and H_2S as well as other substances less frequently present in the environment as a result of industrial emission, such as HNO_3, $H_{2Y}SO_4$ and HCl, form acids in aqueous solution. In the vernacular, they make "acid rain".

At the present time, it does not appear that there are any direct human health effects from acid rain per se, although there may

Table 7. Alberta air quality standards - Hydrogen Sulphide

Contaminant	Alberta Standards ppm	(g/m^3)
24-hour average	0.003	(4)
1-hour average	0.010	(14)
0.5-hour average	0.012	(17)
Occupational exposure limit (8 hour)	10.000	(14,000)
Short-term occupational exposure limit (15 min.)	15.000	(21,000)

be some indirect effects. For example, there are anecdotal reports of eye irritation in bathers swimming in acidified lakes in Ontario. There is currently a study underway in Toronto in which rabbits' eyes are being exposed to acidified lake water to examine this hypothesis. Results are expected in April 1982. Second, there is the effect on leaching of metals into acidified ground water. High mercury levels found in a number of northern Ontario lakes have been attributed to this cause. More recently similar concerns have arisen respecting the leaching of lead.

Finally, there is potentially an effect on the sulphur-selenium balance in the soil. However, while depletion of selenium may result in white muscle disease in cattle and other animals subsisting on vegetation growing on selenium deficient soil, it would be unlikely to ever be a problem in man. Humans normally have enough selenium in their omnivorous diet, much of which originates in areas in Canada or the United States where the soil selenium levels are satisfactory.

4. PRIORITIES FOR ACTION

Where do we go from here? What are the future directions for research and priorities for action?

Number one is the development of local expertise in the area of health effects of acid forming gases, and of environmental pollution generally. There has been a good start in this direction with the formation of the APIGEC/SCAGE Subcommittee on Human and Animal Health, which brought together some of the most interested health professionals in the Province. Regretfully, this committee is presently in a dormant stage. Such groups should be fostered and encouraged to become more knowledgeable in the field. In order to develop a knowledge base upon which to build further, it would be most efficient to bring in experts from out-of-province, around whom a conference or workshop could be designed. This workshop would deal specifically with the health effects of acid forming gases.

The second priority would be the meticulous evaluation of ambient levels of acid forming gases in the Province of Alberta to identify those areas where health effects may be found. Further studies could then be carried out on health problems in these communities in comparison to similar communities or population groups with significantly lower levels.

Finally, even if no problem areas were identified in this way, it would be desirable to look carefully at those areas where there is a potential for higher ambient levels of acid forming gases in the future. Epidemiological surveillance in such communities could usefully be started now so that long-term secular trends in health risks can be correlated with environmental exposure levels in the future.

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THE EFFECTS OF ENVIRONMENTAL SULPHUR ON FARM ANIMALS:
A START FOR DISCUSSION

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ABSTRACT

Many people in the agricultural community of Alberta perceive a connection between sulphur-containing emissions from sour gas plants and the occurence of certain diseases in cattle. These diseases include trace mineral deficiencies, decreased growth rates, reduced fertility, lowered milk yields, lameness, eye irritations, diarrhea, digestive diseases and increased frequency of respiratory problems. This paper describes the problem and identifies groups of factors for consideration in an interdisciplinary approach to this question. It is suggested that the problem be defined, boundaries set and objectives established in order to identify the right questions to be answered in an investigation.

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1. INTRODUCTION

"Truth is so large a target that nobody can wholly miss hitting it, but at the same time, nobody can hit all of it with one throw."

Aristotle

Determination of the possible effects of environmental sulphur on farm animals is a complex problem, demanding of resources and time. Nobility of purpose does not compensate for inadequacy of information. Good science consists not so much in knowing the right answers as in asking the right questions.

The purpose of this paper is not to provide specific answers but rather to initiate discussion leading to a definition of the problem and identification of those "right questions". The paper has three major sections. The first states the problem and suggests three aspects from which the problem may be viewed. The second identifies those factors that should be considered in a scientific interdisciplinary approach to this complex problem. The third outlines a possible strategy to identify the "right questions".

2. STATEMENT OF THE PROBLEM

"It is quite a three-pipe problem".

Arthur Conan Doyle

2.1 PERCEIVED PROBLEM

Many people in rural Alberta perceive a connection between sulphur-containing emissions and the occurence of certain diseases in cattle and sometimes also in themselves. These diseases include selenium deficiency, decreased growth rates, reduced fertility, lowered milk yields, lameness, eye irritations, diarrhea, digestive diseases and increased frequency of respiratory problems. Copper deficiencies have also been observed. Concern has been focused on cases near sour gas processing plants, although similar diseases have been reported from areas not adjacent to processing plants.

2.2 SULPHUR, SELENIUM, COPPER

In Alberta sulphur may be derived from natural sources, emitted from industrial sources such as sour gas plants and fossil fuel plants or applied as fertilizers. Sulphur as sulphate acts antagonistically with both selenium and copper, protecting against selenosis and cuprosis.

Between 40 and 90% of inhaled sulphur dioxide is absorbed in the upper respiratory tract. The deposition pattern in the lung of particulate sulphate varies with aerodynamic size, shape, density and air flow. In general, sulphuric acid aerosols and some sulphate salts, such as zinc ammonium sulphate, are more irritating to the respiratory tract than is sulphur dioxide. Except at very high concentrations, where the absorptive capacity of the upper airways has been overwhelmed, very little sulphur dioxide reaches the lungs directly. At these high concentrations laryngotracheal and pulmonary oedema, and death, may occur. At lower concentrations there may be changes in pulmonary function following single exposure; however no proven effects have been demonstrated at ambient levels. Responses to chronic exposure range from virtually no effects to morphological and inflammatory changes in tissues of the respiratory tract, altered clearance pathways and enzyme activities, and increased pulmonary flow resistance.

The net effect of environmental and biological actions is to convert selenium to inert and insoluble forms such as elemental selenium, metallic selenides, or complexes of selenite with ferric oxides. In areas of acid or neutral soils the amount of biologically available selenium would be expected to decline steadily. In dry areas with alkaline soils and oxidizing conditions, elemental selenium and selenides may be oxidized at a sufficent rate to maintain the availability of biologically active selenium. There are differences in absorption and metabolism of selenium in monogastric and ruminant animals due to the effects of rumen physiology in the latter. Deficiency symptoms reported in ruminants include nutritional myopathy (white muscle disease), lameness, stiffness, abortions, infertility and neonatal mortality. Selenium interacts with sulphur, copper, cobalt and vitamin E and complexes with cadmium, mercury and copper. The element is an essential part of seleno-dependent enzymes such as certain glutathione peroxidases.

The metabolism of copper is complex because of its varied biological functions and interactions with other trace elements such as molybdenum, zinc, iron, cobalt, managanese and the sulphate ion. Copper deficiency may result in anaemia; defects in pigmentation, bone formation, reproduction and myelinization; and reduced growth. The inter-relationships of copper, molybdenum and sulphate ion are more marked in ruminant than in monogastric animals.

It appears that soil acidity may affect the availability of essential trace elements, such as selenium and copper, to feedstuffs, such as grass and hay, eaten by livestock.

More awareness by farmers, veterinarians and agrologists, changing farming practices, more intensive management, genetic selection of livestock for increased production and improved diagnostic and analytical methods, may influence the diagnosis or detection of trace mineral deficiences.

2.3 THREE ASPECTS OF THE PROBLEM

A problem perceived does not mean necessarily that a problem exists. The perceived problem of the possible effects of environmental sulphur on farm animals might be considered as having three components:

1. health,
2. social,
3. political.

The health component comprises definition of the postulated effects on farm animals as outlined previously; elucidation of the direct and indirect aetiologies of these effects; and evaluation to discern whether the perceived problem coincides with the existence of an observed problem. In the event that perception and observation coincide, then there must be demonstration of a dose-related cause-effect relationship, as well as prediction of effects and recommendations for amelioration of the problem.

The social component consists of the perception of the problem by society; the acceptability of risk by all of society (or an at-risk portion thereof) for agriculture, energy production and the environment; and the motivation for action.

The political component includes the economics of the agricultural and energy industries; changes in industrial practices and technologies; as well as guidelines and regulations.

That these three components may not be in accord should not detract from the contiguity that exists. However, it is the intention of this paper to consider only the health component. Statement of the problem is the first step. It is also helpful to designate boundaries that delineate the extent of the problem under consideration.

3. FACTORS TO BE CONSIDERED IN A SCIENTIFIC APPROACH TO HEALTH EFFECTS

> "What I tell you three times is true".
>
> Lewis Carroll

Since we are not hunting the Snark we must employ more scientific methods. A number of systems are associated with the problem and should be considered:

1. farm animals,
2. agricultural crops and forages,
3. agricultural soils,
4. air.

It is apparent that these systems interact one with another. The factors and considerations for each system are reviewed briefly.

3.1 FARM ANIMALS

The problem focuses on the following diseases of cattle:

1. trace element deficiencies, including nutritional myopathy, neonatal weakness or mortality;
2. reproductive abnormalities, including fewer live calves, prolonged calving interval, decreased ratio of cows bred to calves weaned, abortions;
3. reduced productivity, including lowered milk yields in dairy cattle and reduced growth in beef cattle;
4. lameness and stiffness;
5. diarrhea;
6. increased susceptibility to infection; e.g. respiratory diseases.

Each of these conditions requires definition in order to properly distinguish the "affected" group from the "normal" group. Definition would also facilitate agreement on incidence, diagnosis, determination of aetiologies, and understanding of the perceived problem.

Many of these diseases have more than one possible cause. In some instances it is relatively easy to identify the cause, in others the cause is frequently not determined despite considerable effort. Acquisition of information to assist in the differential diagnosis of each of the defined diseases is essential. This information should include nutrition, animal husbandry, breeding history and health records. The partial or complete lack of farm records would prevent a retrospective study and would hinder determination of the cause of many of the diseases listed above.

Management is an important factor in the economic, health and productive aspects of farm operation. The quality of management has considerable influence on the well-being of both dairy and beef operations.

Epidemiological studies are a means through which a higher-than-predicted incidence of a disease could be identified; this could be on a regional or local basis. It would also be necessary to review historical data, since the effects may be a result of small annual incremental changes. Again, the quality of record-keeping is a major factor in the usefulness of an epidemiological study.

It is necessary to define these effects and to establish how they occur and to determine whether sulphur is involved.

3.2 AGRICULTURAL CROPS AND FORAGES

This refers to the crops ingested by livestock and therefore focuses on the nutrient and non-nutrient values of these crops. Normal growth, production and reproduction of livestock depends upon adequate concentrations and amounts of required nutrients in the plants consumed. The major dietary nutrient categories for ruminant animals include protein, energy, water, fibre, major mineral elements, trace elements and three fat-soluble vitamins A, D, and E. Relative or absolute deficiencies or excesses in these nutrients can produce an array of symptoms ranging from simple growth reduction to disease and death.

Sulphur emissions have been suggested as a possible link between trace element malnutrition and some cattle diseases. Selenium deficiency has been identified for particular attention in this regard.

With reference to animal nutritional requirements, copper, molybdenum, manganese and zinc have been shown to be at marginal levels in certain crops grown in Alberta. At the same time plant sulphur levels also were marginal to deficient for animal production.

Plants are the primary source of minerals for livestock. The mineral concentrations present in plants vary with species, soil characteristics, season, climate, level of fertilization and stage of maturity. Further, the influences of these factors on mineral levels may also be affected by the use of pesticides, and harvesting and grazing practices. Soil composition is considered to be the major factor influencing trace element levels in plants. Decreases in trace element concentrations with advancing plant maturity is of considerable significance in areas where trace element concentrations are marginal.

An assessment of plant trace element status should include the following:

1. determination of concentrations and bioavailability of sulphur, copper, molybdenum, manganese, selenium and zinc;
2. determination of changes in concentrations of these elements within and between plant species over seasons, between locations, and under different climatic conditions;
3. comparison of plant concentrations with animal requirements.

Major factors affecting results would be the sampling precedures by inadequately estimating the population being sampled, and the adequacy, availability, capability, and cost of suitable chemical analytical procedures for these minerals.

3.3 AGRICULTURAL SOILS

Natural soil formation processes tend toward the acid state. The addition of anthropogenic acid precursors, such as nitrogen fertilizer and the oxides of nitrogen and sulphur, may serve to accelerate these processes. Soils developed under arid climates are near neutral or alkaline in reaction and contain free calcium carbonate. Acid additions are not likely to make any significant pH changes for a long time. In more humid zones soils are somewhat acidic, contain no free calcium carbonate and will be very responsive to acid additions.

Soil acidification can result in the following soil changes:

1. accelerated leaching of essential bases and nutrients;
2. mineral degradation and transformation;
3. a reduction in cation exchange capacity;
4. a reduction in base saturation;
5. a reduction in pH;
6. an increase in the mobility of fulvic acids;
7. a reduction in the microbiological activity in the soils and therefore a reduction in the rate of re-cycling of bases and nutrients.
8. a modification of availability of elements.

The soil changes listed above are expected to be reflected in the quantity and quality of crops and subsequently the health of the animals utilizing these crops. This complex relationship should be investigated during the preliminary phase of this study and an attempt made to forecast the effects of additional acid deposition on some soil characteristics.

The sampling procedures for soils and crops and forages must be developed in such a manner that it is possible to correlate the results of soil chemical analyses with those obtained from crops and forages. This correlation between soil analyses, plant analyses and animal analyses is crucial.

3.4 AIR

Most of the industrial emissions of sulphur are in the form of sulphur dioxide. This gas may be transformed subsequently to other sulphur compounds by thermal or photochemical reactions. The form of the sulphur determines whether interaction with animals, plants or soil, is benefical or deleterious when the transported material returns to ground as wet or dry deposition. Transport and deposition varies with source characteristics, wind speed and direction, atmospheric stability, rainfall, vertical temperature gradients,geography and topography.

The point source release of sulphur dioxide is quantifiable. This information, together with climatological and physico-chemical data, can be used to develop a simple diffusion model for a first order estimate of sulphur deposition eminating from a point source. Verification of this estimate requires the determination of wet and dry deposition and of ambient air concentrations of sulphur compounds. These determinations should be both qualitative and quantitative as it is the product which reacts with animal, plant or soil that is of immediate interest. It would also be necessary to demonstrate movement of the suspect emission from a point source to a specific site at which a possible effect might be induced in an animal. Techniques for measurement of wet and dry deposition and methods for analysis of sulphur compounds should also be considered.

3.5 INTERACTIONS

Although the perceived problem has been expressed in terms of sulphur, neither the possibility of additive, synergistic or inhibitory interactions with other compounds nor alternate aetiologies can be ignored. At this time there is insufficient information relating the possible cause to this perceived problem and to possible direct or indirect mechanisms of action.

4. A POSSIBLE APPROACH

> "You go back and forth from observation to theory. You don't know what to look for without a theory; and you can't check the theory without looking at the fact; and the fact is only meaningful in the light of some theoretical construction."
>
> Joshua Lederberg

Many promising research projects have ultimately proved worthless because the complexity of the problem was allowed to swamp the subsequent investigation, with the result that it was impossible to derive solutions. Conversely, solutions based on a superficial understanding of a problem may be expedient but, in the long run, may become an embarrassment.

There are several phases in the approach to this problem.

4.1 PHASE ONE: DEFINITION AND BOUNDING OF THE EXTENT OF THE PROBLEM

It is necessary to simplify the problem to a point at which it is likely to be capable of analytical solution. The problem might be expressed in the form of a question, for example:

> Are sulphur-containing emissions the cause of certain diseases and trace element deficiences of cattle in Alberta?
>
> or
>
> Why do certain diseases and trace element deficiences of cattle occur in Alberta?

Although similar, these two questions differ in emphasis. Thus the definition of the problem is important, for this will influence all subsequent work. At this stage it would be helpful to define the biological effects in cattle and the inputs of sulphur into farming. It may also be necessary to conduct pilot field and laboratory studies and herd investigations to eliminate those diseases of proven aetiologies and to identify and quantify sources of sulphur.

Boundaries for the extent of the problem are necessary in order to focus the investigation and prevent diffusion of effort. This helps to clarify the problem to be investigated and give direction to the investigation.

4.2 PHASE TWO: IDENTIFICATION OF OBJECTIVES

Arising out of phase one it should be possible to establish the objectives of the investigation. Overall objectives might include:

1. to determine the role of sulphur in the aetiology of trace element deficiencies and certain diseases of cattle in Alberta;
2. to determine if direct exposure to sulphur-containing emissions affects the health and productivity of cattle in Alberta;
3. to determine if indirect exposure to sulphur-containing emissions affects the health and productivity of cattle in Alberta;
4. to determine the causes of certain specified diseases and trace element deficiencies affecting cattle in Alberta.

In a project of this size there will develop a hierarchy of major and minor objectives. It is then possible to determine priorities.

4.3 PHASE THREE: DESIGN OF EXPERIMENTAL PROTOCOLS

Having defined the problem, set boundaries, stated objectives and set priorities, it is then possible to generate a number of questions to be answered and hypotheses to be tested.

It is to be hoped that the "right questions" have been asked. The hypotheses require testing to determine if they stand or fall.

Development of the experimental designs is a critical stage. Considerable data may be needed to permit subtle differences to pierce the veil of random variation. It is salutory to remember that one who seeks what is not there will "find" it only if the experimental data are insufficient or logic discarded. Thus an experiment of insuffícent size will be the source of much arguement about conflicting or ambiguous results.

4.4 PHASE FOUR: IMPLEMENTATION

This is a major phase. The research will be conducted by a team of scientists from many disciplines, utilize both field and laboratory studies, require the cooperation of the agricultural community and segments of the energy industry, involve both conventional and innovative procedures, and will not be accomplished overnight.

4.5 EXAMPLE OF THE EXPERIMENTAL APPROACH

The following example may serve to illustrate this experimental approach.

Phase One: In this example there is concern that sulphur emissions decrease the resistance of dairy cattle to respiratory diseases. This may be expressed as a question:

> Does the inhalation of sulphur dioxide at
> ambient levels decrease the resistance of
> dairy cattle to respiratory diseases?

Before proceeding further it may be necessary to ascertain two things: the ambient levels of sulphur dioxide and the incidence of respiratory diseases in dairy cattle. The means for these parameters may estimate a wide range of individual values, emphasizing the importance of experimental design to distinguish between subtle differences and random variation.

Phase Two: An objective might be:

> To determine if inhalation of sulphur dioxide at 2 ppm depresses the immune response of dairy cattle to respiratory infections.

Sub-objectives may refer to bacterial or viral respiratory pathogens; age, sex or breed of cattle; or geographical location.

Phase Three: Some experimental designs that might be considered include:

1. monitoring of dairy herds, in areas of zero (0 ppm) and high (2 ppm) air concentrations of sulphur dioxide, for
    a. incidence and type of respiratory diseases,
    b. pulmonary function and clearance,
    c. nutrition status,
    d. management of herd;
2. laboratory exposure of cattle to various levels of sulphur dioxide, with and without challenge by pathogens, and detailed investigation of the bovine immune response.

In this example it is important to note that the original question excluded consideration of other airborne agents, such as ozone, that could be involved. Further, the objective in this example fails to consider fluctuating levels of sulphur dioxide, which might be more representative of natural occurring conditions. Lastly, the protocols do not recognize the cost of research with cattle. These omissions would be irrelevant if, at phase one, the additional information demonstrated that there was no difference in the incidence of respiratory diseases in cattle from areas with different ambient levels of sulphur dioxide.

5. CONCLUSION

> "Life is the art of drawing sufficient conclusions from insufficient premises".
>
> Samuel Butler

The possible effects of environmental sulphur on farm animals form a complex problem. It requires considerable mental effort, interdisciplinary cooperation and clear thinking. The perceived problem arose because of the extraction and partial release of sulphur from natural gas into the environment. This same natural gas was largely derived from the bodies of plants and other living things that have become chemically stabilized after undergoing partial decomposition. Burning of gas completes the recycling process. Thus, we study today the effects of pollution that occurred a long time ago.

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THE EFFECTS OF ENVIRONMENTAL SULPHUR ON FARM ANIMALS: A PILOT STUDY

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ABSTRACT

Many people in the agricultural community of Alberta perceive a connection between sulphur-containing emissions from sour gas plants and the occurence of certain diseases in cattle. These diseases include trace mineral deficiencies, decreased growth rates, reduced fertility, lowered milk yields, lameness, eye irritations, diarrhea, digestive diseases and increased frequency of respiratory problems. This paper presents the findings of an interdisciplinary pilot study conducted in the Rocky Mountain House area in 1981.

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1. INTRODUCTION

This paper continues the same topic discussed at this Symposium by Prior and co-workers (1982) entitled "The Effects of Environmental Sulphur: A Start for Discussion."

The purpose of this interdisciplinary pilot study into the possible effects of environmental sulphur on farm animals was threefold:

1. To define the perceived problem in order to facilitate investigation;
2. To identify those "right questions"; the answers to which would lead to elucidation of the perceived problem;
3. To establish the processes required for interdisciplinary research.

2. MATERIALS AND METHODS

Two dairy and two beef farms in the Rocky Mountain House area were identified as having problems with livestock perceived to be connected with emissions from neighbouring sour gas plants. These problems included:

1. Trace element deficiences; including nutritional myopathy, neonatal weakness or mortality;
2. Reproductive abnormalities, including fewer live calves, prolonged calving intervals, decreased ratio of cows bred to calves weaned, silent oestrus;
3. Decreased milk yields or weight gains.

The two dairy (A,B) and two beef (C,D) farms were at varying distances from Rocky Mountain House and the sour gas processing plants at Strachan (Gulf) and Ram River (Canterra). Field trips were made to collect samples of pastures, stored feeds, grains and soils for chemical analysis; to locate lead acetate candles, Huey plates and dustfall jars on the sites for measurement of sulphur in the air; collect bovine blood samples for chemical and biochemical analysis; and to obtain epidemiological information.

The pasture, stored feed and grain samples were collected from 1 m² areas as described by Westra (1982) and analyzed for macro- and micro-nutrients also as described by Westra (1982). Soil samples were taken from sites beside selected grass sampling cages. Each soil sample was made from three subsamples taken from depths of 0 to 8, 8 to 18, 18 to 30, 30 to 60, 60 to 90 and 90 to 120 cm.

Soil pH was determined on a 2:1 water-soil paste. Electrical conductivity and water-soluble ions were determined on the paste extracts; sodium and potassium by flame photometry; calcium and magnesium by atomic absorption; carbonate and bicarbonate by acid titration; and sulphate and chloride by colorimetry. Total sulphur was determined by combustion and infrared detection; total carbon by a combustion-gasometric method; and carbonate-carbon by a gasometric method. Ammonium acetate was used to determine extractable cations and cation exchange capacity. Nitrate and ammonium nitrogen was measured by colorimetry; and total nitrogen was determined by a macro-Kjeldahl method. Metals were extracted with DTPA-TEA and measured by atomic absorption.

Air quality was monitored by Huey plates, lead dioxide (SO_2) candles and zinc acetate (H_2S) candles. Analysis was by a wet chemical volumetric procedure, ion chromatography or atomic absorption according to the particular sampler. Bovine glutathione peroxidase activity was assayed by the method of Board and Peter (1976) and Peter (1980) and blood selenium will be determined by atomic absorption by modification of the method of Clinton (1977).

Total annual sulphur deposition within 50 km of the Strachan and Ram River gas plants was estimated using the SULDEP computer code (Alberta Environment 1982). The mathematical model (Western Research & Development 1978) assumes that:

1. The plume has a rectangular shape;
2. No significant chemical transformations occur;
3. Dry deposition is given by the product of ambient ground-level concentrations and a stability dependent dry deposition velocity;
4. Wet deposition is given by the product of ambient ground-level concentrations and the ratio between precipitation rate and a temperaure dependent solubulity parameter.

Design values were used for sulphur dioxide emission rates, stack gas exit speed and stack gas exit temperature. The joint frequencies of wind speed, wind direction and stability were from the Rocky Mountain House airport weather station for the years 1968 to 1977.

3. RESULTS AND DISCUSSION

3.1 PLANT SAMPLES

The results of the analyses of plant samples of pastures, stored feeds and grains for macro-and micro-nutrients are summarized in

Table 1. Summary of means (± standard deviations) of analyses of pastures, feeds and grains from each of four farms in the Rocky Mountain House area.

Parameter (Dry Matter basis)	Pasture(P) or Feed(F) or Grains(G)	Farm			
		A	B	C	D
(%)					
Dry Matter (DM)	P	94.4±0.7	93.6±0.9	94.6±0.9	93.6±0.8
	F	88.4	85.9±1.6	80.5±9.9	77.3±7.7
	G	89.3±0.7	89.3±0.8	90.2±0.6	84.9±2.7
Crude Protein (CP)	P	11.9±1.6	19.4±2.6	18.1±8.3	22.1±0.9
	F	12.2	11.4±1.6	9.7±1.2	11.3±3.4
	G	13.9±0.7	13.9±1.6	10.0±1.1	12.4±0.8
Nitrates (NIT)	P	0.02±0.04	0.10±0.10	0.09±0.20	0.01±0.02
	F	0	0.01±0.03	0.04±0.05	0.25±0.54
	G	-	-	-	-
Acid Detergent Fibre(ADF)	P	35.2±2.9	32.3±3.8	32.5±9.0	30.4±2.3
	F	37.1	40.9±2.1	48.9±0.1	39.2±4.2
	G	-	-	-	-
Calcium (Ca)	P	0.75±0.09	0.95±0.28	0.65±0.06	0.87±0.27
	F	0.84	0.97±0.20	0.67±0.18	0.54±0.19
	G	0.05±0.01	0.07±0.01	0.06±0.01	0.07±0.02
Phosphorus (P)	P	0.20±0.03	0.38±0.04	0.30±0.07	0.36±0.03
	F	0.20	0.18±0.03	0.19±0.01	0.16±0.08
	G	0.41±0.05	0.07±0.01	0.35±0.04	0.07±0.02
Sulphur (S)	P	0.16±0.03	0.22±0.07	0.17±0.07	0.23±0.05
	F	0.12	0.09±0.02	0.07±0.01	0.15±0.05
	G	0.08±0.00	0.07±0.01	0.09±0.01	0.09±0.01
Magnesium (Mg)	P	0.19±0.02	0.21±0.03	0.17±0.02	0.21±0.05
	F	0.18	0.20±0.04	0.20±0.03	0.15±0.03
	G	0.14±0.02	0.15±0.01	0.12±0.01	0.15±0.01
Sodium (Na)	P	0.015±0.011	0.015±0.009	0.025±0.015	0.017±0.009
	F	0.024	0.009±0.003	0.007±0.0	0.010±0.004
	G	0.006±0.001	0.006±0.002	0.005±0.004	0.006±0.003
Potassium (K)	P	1.76±0.44	2.74±0.45	2.22±1.01	3.06±0.41
	F	1.79	1.77±0.30	1.71±0.13	2.41±0.78
	G	0.47±0.08	0.58±0.02	0.53±0.04	0.53±0.02

continued ...

Table 1 (Continued).

(ppm)		A	B	C	D
Iron (Fe)	P	327±358	205±145	776±688	363±266
	F	90	72± 18	90± 36	186±306
	G	41± 4	46± 0	56± 2	57± 13
Manganese (Mn)	P	47± 5	68± 13	80± 27	76± 15
	F	49	52± 8	61± 15	68± 29
	G	31± 17	34± 21	61± 9	40± 28
Copper (Cu)	P	8.8±1.3	13.1±6.7	18.1±10.3	21.0±7.2
	F	6.3	8.7±3.3	7.9± 2.3	9.8±5.4
	G	8.2±2.9	8.4±3.7	14.0± 4.2	9.6±4.0
Zinc (Zn)	P	21±1	40±30	24±4	43±16
	F	20	20± 4	19±1	25± 5
	G	36±5	38± 1	28±6	39± 2
Selenium (Se)	P	0.032±0.005	0.041±0.016	0.059±0.026	0.072±0.037
	F	0.153	0.139±0.059	0.531±0.630	0.427±0.272
	G	0.018±0.006	0.008±0.002	0.019±0.004	0.036±0.001
Molybdenum (Mo)	P	3.58±0.64	2.13±0.27	2.16±0.75	1.41±0.20
	F	1.22	2.19±1.86	0.69±0.42	1.45±0.67
	G	1.01±0.23	0.93±0.08	0.69±0.06	0.76±0.10
Boron (B)	P	12.9±3.1	14.9±2.2	11.1±4.9	16.2±4.3
	F	13.5	15.0±1.9	11.3±3.0	10.4±4.6
	G	1.0±0.1	1.1±0.1	0.8±0.1	1.0±0.1
Aluminium (Al)	P	103±43	234±128	754±688	370±338
	F	68	47± 17	43± 4	230±400
	G	16± 4	12± 1	10± 1	33± 7
Cobalt (Co)	P	0.12±0.04	0.29±0.13	0.72±0.63	0.36±0.22
	F	0.27	0.37±0.05	0.37±0.17	0.35±0.28
	G	0.40±0.07	0.46±0.06	0.35±0.05	0.43±0.06
Chromium (Cr)	P	0.67±0.33	1.04±0.53	1.28±0.80	1.00±0.73
	F	1.23	1.48±0.55	1.57±0.48	1.90±0.88
	G	1.66±0.18	1.32±0.28	1.09±0.20	1.37±0.13
Arsenic (As)	P	0.31±0.33	0.73±0.26	1.77±1.40	1.26±0.53
	F	-	-	-	-
	G	-	-	-	-
Lead (Pb)	P	1.45±0.10	1.99±0.67	1.38±0.58	2.03±0.33
	F	1.39	2.20±0.37	3.01±0.66	2.13±0.83
	G	2.24±0.10	2.98±0.60	2.25±0.30	2.54±0.83

continued ...

Table 1 (Concluded).

		A	B	C	D
Cadmium	P	0.19±0.30	0.11±0.05	0.16±0.09	0.19±0.04
(Cd)	F	0.24	0.26±0.02	0.31±0.20	0.26±0.10
	G	0.24±0.01	0.28±0.02	0.22±0.04	0.25±0.03
Vanadium	P	0.25±0.15	0.58±0.32	1.44±1.22	0.88±0.72
(V)	F	1.31	1.70±0.24	1.38±0.01	1.33±0.93
	G	1.73±0.05	1.46±0.11	1.06±0.01	0.75±0.02
Strontium	P	25.3±3.2	17.7± 4.8	11.5±1.5	14.3±2.6
(Sr)	F	20.7	29.8±18.5	19.1±2.7	11.0±3.2
	G	1.6±0	1.4± 0.1	1.3±0.3	1.5±0.2

Table 1. These findings are interpreted with respect to animal nutrition requirements for dairy and beef cattle (ARC 1980, NRC 1975, NRC 1978, Westra, 1982) as outlined in Table 2.

Samples from pastures from all farms were low in selenium and marginal to low for zinc. Copper levels were low on one farm, as was crude protein. The nitrogen:sulphur ratios ranged from 11.9 to 17.0, the recommended ratio is usually given as 10:1 for cattle.

Samples of stored feeds were low in copper and zinc; levels of sulphur were low on two farms. Nitrogen:sulphur ratios ranged from 12.1 to 22.0. Samples of grains from all farms were low in sulphur and selenium, and samples, from three farms were also low in copper. Nitrogen:sulphur ratios ranged from 17.7 to 27.8.

These findings suggest that cattle feeding solely on these pastures, stored feeds and grains might develop trace mineral deficiencies with time.

Table 2. Requirements for certain macro- and micro-nutrients by cattle.[1]

Mineral	NRC (1978) Dairy	NRC (1975) Beef	ARC (1980) Cattle	Reccommended Levels for Alberta (Westra 1982)
%				
Calcium	0.37-0.60	0.81-0.76	0.17-0.67	0.2-0.6
Phosphorus	0.26-0.40	0.18-0.54	0.11-0.35	0.2-0.4
Magnesium	0.16-0.20	0.04-0.10	0.12-0.21	0.1-0.2
Potassium	0.8	0.6-0.8		0.8
Sodium	0.10-0.18	0.6	0.05-0.20	0.1-0.18
Sulphur (ppm)	0.16-0.20	0.1	0.11-0.16	0.1-0.2
Selenium	0.1	0.05-0.10	0.05-0.10	0.1
Copper	10	4	8-20	10
Manganese	40	1-20	10-25	40
Zinc	40	20-30	12-34	50
Molybdenum				0.5
Iron	50	10	30-40	50

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[1] The range of requirements includes growing animals, mature and lactating cows. All values given on a dry matter basis.

3.2 SOIL SAMPLES

A summary description of the soils sampled on each farm is given in Table 3. The results of the soil analyses are summarized in Table 4.

Table 3. Summary description of the soils sampled from four farms in the Rocky Mountain House area.

Farm	Description of soils
A	Orthic Humic Gleysol tending at some sites to Humic Luvic Gleysol developed from morainal (with surficial lacustrine-like features) materials; moderately well to poorly drained; lower slope and depressional positions sampled.
B	Orthic Gray Luvisol tending to Podzolic Gray Luvisol developed from morainal (with surficial lacustrine-like features) materials; well drained; sampled along slope gradient from upper to lower slope positions.
C	Orthic Gray Luvisol tending to Podzolic Gray Luvisol developed from lacustrine materials; well drained; sampled upper slope positions.
D	Orthic Regosol, except Pozolic Gray Luvisol at Site 1, developed from recent alluvium, except glacio-fluvial materials at Site 1; well drained; sampled middle and upper slope positions.

Table 4. Summary of means (± standard deviations) of soil characteristics of a small selected area from each of four farms in the Rocky Mountain House area.

Parameter	Sample depth (cm)	Farm A	B	C	D
pH of 2:1 water-soil paste	0- 8	6.9^{a} ± 0.2[1]	6.4^{a} ± 0.4	6.5^{a} ± 0.3	6.0^{a} ± 0.2
	8- 18	7.0^{a} ± 0.4	6.8^{a} ± 0.4	6.8^{a} ± 0.2	6.1^{a} ± 0.1
	18- 30	7.3^{a} ± 0.5	6.8^{a} ± 0.5	6.8^{a} ± 0.3	6.4^{a} ± 0.1
	30- 60	7.5^{a} ± 0.4	6.8^{a} ± 0.3	7.0^{a} ± 0.4	6.6^{a} ± 0.3
	60- 90	7.6^{a} ± 0.4	7.5^{a} ± 0.2	7.5^{a} ± 0.2	6.8^{a} ± 0.2
	90-120	7.6^{a} ± 0.4	7.8^{a} ± 0.2	7.9^{a} ± 0.1	7.2^{a} ± 0.2
EC mS/cm	0- 8	0.77^{a} ± 0.29	0.48^{a} ± 0.18	0.38^{a} ± 0.07	0.58^{a} ± 0.13
	8- 18	0.56^{b} ± 0.20	0.16^{a} ± 0.08	0.12^{a} ± 0.01	0.20^{ab} ±0.03
	18- 30	0.36^{a} ± 0.26	0.08^{a} ± 0.02	0.18^{a} ± 0.21	0.14^{a} ± 0.05
	30- 60	0.17^{a} ± 0.11	0.22^{a} ± 0.02	0.16^{a} ± 0.09	0.14^{a} ± 0.07
	60- 90	0.14^{a} ± 0.05	0.16^{a} ± 0.02	0.20^{a} ± 0.02	0.18^{a} ± 0.06
	90-120	0.11^{a} ± 0.03	0.24^{b} ± 0.04	0.21^{b} ± 0.01	0.19^{ab} ±0.02
SAR	0- 8	0.20^{a} ± 0.04	0.08^{a} ± 0.02	0.10^{a} ± 0.03	0.19^{a} ± 0.15
	8- 18	0.31^{a} ± 0.12	0.10^{a} ± 0.03	0.15^{a} ± 0.05	0.19^{a} ± 0.02
	18- 30	0.52^{a} ± 0.28	0.15^{a} ± 0.04	0.17^{a} ± 0.01	0.13^{a} ± 0.03
	30- 60	0.43^{a} ± 0.26	0.10^{a} ± 0.04	0.14^{a} ± 0.05	0.12^{a} ± 0.04
	60- 90	0.42^{a} ± 0.32	0.10^{a} ± 0.00	0.10^{a} ± 0.00	0.12^{a} ± 0.03
	90-120	0.37^{a} ± 0.18	0.08^{a} ± 0.01	0.09^{a} ± 0.01	0.10^{a} ± 0.01
Water-soluble ions (extract from 2.1 water-soil paste)					
Ca me/L	0- 8	7.2^{a} ± 2.5	4.3^{a} ± 1.4	2.8^{a} ± 0.4	4.0^{a} ± 0.9
	8- 18	5.6^{b} ± 1.7	1.9^{a} ± 0.8	1.0^{a} ± 0.1	1.7^{a} ± 0.3
	18- 30	3.8^{a} ± 3.0	0.9^{a} ± 0.4	0.5^{a} ± 0.1	1.1^{a} ± 0.3
	30- 60	1.5^{a} ± 0.9	2.2^{a} ± 0.4	1.2^{a} ± 0.7	1.1^{a} ± 0.5
	60- 90	1.0^{a} ± 0.5	1.6^{a} ± 0.2	1.5^{a} ± 0.1	1.4^{a} ± 0.5
	90-120	0.9^{a} ± 0.4	2.2^{b} ± 0.2	1.6^{ab} ± 0.1	1.4^{ab} ± 0.3
Mg me/L	0- 8	2.0^{a} ± 1.3	1.1^{a} ± 0.3	0.8^{a} ± 0.1	1.9^{a} ± 0.6
	8- 18	1.6^{a} ± 0.8	0.4^{a} ± 0.2	0.2^{a} ± 0.1	0.7^{a} ± 0.2
	18- 30	0.8^{a} ± 0.5	0.2^{a} ± 0.2	0.2^{a} ± 0.1	0.5^{a} ± 0.2
	30- 60	0.6^{a} ± 0.3	0.6^{a} ± 0.1	0.5^{a} ± 0.3	0.5^{a} ± 0.3
	60- 90	0.4^{a} ± 0.2	0.5^{a} ± 0.2	0.5^{a} ± 0.1	0.6^{a} ± 0.2
	90-120	0.4^{a} ± 0.1	0.9^{a} ± 0.6	0.6^{a} ± 0.2	0.7^{a} ± 0.1
Na me/L	0- 8	0.4^{a} ± 0.1	0.1^{a} ± 0.1	0.1^{a} ± 0.1	0.2^{a} ± 0.1
	8- 18	0.6^{b} ± 0.3	0.1^{a} ± 0.0	0.1^{a} ± 0.1	0.2^{ab} ± 0.0
	18- 30	0.6^{a} ± 0.3	0.1^{a} ± 0.0	0.1^{a} ± 0.0	0.1^{a} ± 0.0
	30- 60	0.4^{a} ± 0.2	0.1^{a} ± 0.0	0.1^{a} ± 0.0	0.1^{a} ± 0.0
	60- 90	0.4^{a} ± 0.3	$<0.1^{a}$ ± 0.0	0.1^{a} ± 0.0	0.1^{a} ± 0.0
	90-120	0.3^{a} ± 0.2	$<0.1^{a}$ ± 0.0	0.1^{a} ± 0.0	0.1^{a} ± 0.0

continued...

Table 4 (Continued).

		A	B	C	D
K	0- 8	0.20^{a} ± 0.06	0.60^{a} ± 0.31	0.37^{a} ± 0.33	0.52^{a} ± 0.27
me/L	8- 18	0.03^{a} ± 0.03	0.10^{a} ± 0.10	0.04^{a} ± 0.03	0.04^{a} ± 0.02
	18- 30	0.02^{a} ± 0.02	0.06^{a} ± 0.05	0.01^{a} ± 0.01	0.01^{a} ± 0.00
	30- 60	$<0.01^{a}$ ± 0.01	0.10^{a} ± 0.13	0.01^{a} ± 0.01	0.01^{a} ± 0.00
	60- 90	0.01^{a} ± 0.02	0.01^{a} ± 0.00	0.01^{a} ± 0.01	0.01^{a} ± 0.01
	90-120	0.01^{a} ± 0.01	0.00^{a} ± 0.00	0.01^{a} ± 0.01	0.01^{a} ± 0.00
HCO_3&CO_3	0- 8	7.81^{a} ± 2.83	4.62^{a} ± 1.82	3.45^{a} ± 0.87	4.51^{a} ± 0.95
	8- 18	5.96^{b} ± 1.98	2.00^{ab} ±1.09	1.20^{a} ± 0.21	1.77^{a} ± 0.23
me/L	18- 30	3.12^{b} ± 0.96	0.97^{a} ± 0.53	0.75^{a} ± 0.17	1.39^{ab} ±0.52
	30- 60	1.54^{a} ± 0.55	2.80^{a} ± 0.21	1.75^{a} ± 1.07	1.59^{a} ± 0.57
	60- 90	1.31^{a} ± 0.55	1.84^{a} ± 0.20	2.18^{a} ± 0.23	2.13^{a} ± 1.26
	90-120	1.30^{a} ± 0.54	2.24^{a} ± 0.41	2.08^{a} ± 0.20	2.20^{a} ± 1.17
SO_4	0- 8	0.39^{a} ± 0.17	0.32^{a} ± 0.06	0.23^{a} ± 0.12	0.33^{a} ± 0.07
	8- 18	0.38^{a} ± 0.21	0.21^{a} ± 0.02	0.12^{a} ± 0.07	0.15^{a} ± 0.04
me/L	18- 30	0.94^{a} ± 1.40	0.14^{a} ± 0.04	0.08^{a} ± 0.05	0.14^{a} ± 0.06
	30- 60	0.83^{a} ± 1.21	0.14^{a} ± 0.04	0.08^{a} ± 0.07	0.11^{a} ± 0.04
	60- 90	0.42^{a} ± 0.52	0.24^{a} ± 0.05	0.06^{a} ± 0.07	0.07^{a} ± 0.02
	90-120	0.27^{ab} ±0.14	0.68^{b} ± 0.23	0.14^{a} ± 0.04	0.10^{a} ± 0.05
Cl	0- 8	0.16^{a} ± 0.06	0.20^{a} ± 0.09	0.10^{a} ± 0.07	0.22^{a} ± 0.07
me/L	8- 18	0.13^{a} ± 0.16	0.05^{a} ± 0.04	0.03^{a} ± 0.03	0.05^{a} ± 0.04
	18- 30	0.06^{a} ± 0.06	0.01^{a} ± 0.02	0.00^{a} ± 0.00	0.00^{a} ± 0.00
	30- 60	0.00^{a} ± 0.00	0.18^{b} ± 0.06	0.05^{ab} ±0.07	0.00^{a} ± 0.00
	60- 90	0.03^{a} ± 0.06	0.14^{a} ± 0.06	0.02^{a} ± 0.04	0.00^{a} ± 0.00
	90-120	0.04^{a} ± 0.08	0.18^{a} ± 0.15	0.06^{a} ± 0.12	0.19^{a} ± 0.19
CEC	0- 8	75.8^{b} ±16.4	20.8^{a} ± 1.8	17.8^{a} ± 2.0	9.4^{a} ± 5.9
me/100g	8- 18	70.4^{b} ±14.0	19.0^{a} ± 1.6	14.2^{a} ± 1.2	37.4^{a} ±10.1
	18- 30	65.8^{a} ±39.8	22.2^{a} ± 1.2	17.6^{a} ± 5.7	33.0^{a} ± 9.1
	30- 60	23.7^{a} ± 5.7	21.5^{a} ± 1.2	22.6^{a} ± 3.2	32.8^{a} ± 7.4
	60- 90	23.7^{ab} ± 4.9	14.1^{a} ± 1.0	20.3^{ab} ±2.5	32.3^{b} ± 9.2
	90-120	25.6^{ab} ± 1.8	16.0^{a} ± 2.6	17.7^{ab} ±1.0	30.0^{b} ± 7.2
Extractable cations (extracted in 1N NH_4OAc, pH 7)					
Ca	0- 8	59.5^{b} ±10.2	18.2^{a} ± 4.6	12.0^{a} ± 1.4	24.4^{a} ± 5.5
me/100g	8- 18	59.0^{b} ± 8.6	15.6^{a} ± 2.4	9.8^{a} ± 1.2	25.7^{a} ± 6.7
	18- 30	47.1^{b} ±13.7	16.0^{a} ± 0.9	12.0^{a} ± 4.4	21.5^{ab} ±6.5
	30- 60	30.5^{a} ±10.9	19.2^{a} ± 2.5	24.0^{a} ±11.1	24.1^{a} ± 7.8
	60- 90	28.8^{a} ±11.9	38.4^{a} ± 2.1	35.3^{a} ± 1.5	24.1^{a} ± 6.5
	90-120	27.3^{a} ±14.5	40.1^{a} ± 0.5	37.4^{a} ± 0.8	28.8^{a} ± 7.6
Mg	0- 8	8.9^{b} ± 1.3	3.0^{a} ± 0.6	2.1^{a} ± 0.4	5.6^{ab} ± 1.6
me/100g	8- 18	10.1^{b} ± 1.6	2.4^{a} ± 1.7	1.7^{a} ± 0.6	5.8^{ab} ± 2.0
	18- 30	8.0^{a} ± 1.8	3.6^{a} ± 0.4	3.4^{a} ± 1.5	6.2^{a} ± 2.1
	30- 60	5.2^{a} ± 0.7	3.4^{a} ± 0.8	4.5^{a} ± 0.3	7.0^{a} ± 2.3
	60- 90	5.4^{a} ± 1.0	3.2^{a} ± 0.6	4.1^{a} ± 0.2	6.6^{a} ± 2.2
	90-120	5.6^{a} ± 1.1	3.8^{a} ± 1.8	4.5^{a} ± 0.3	6.2^{a} ± 2.0

continued ...

Table 4 (Continued).

		A	B	C	D
Na	0- 8	0.9^{a} ± 0.1	0.6^{a} ± 0.0	0.6^{a} ± 0.0	0.7^{a} ± 0.4
me/100g	8- 18	0.9^{a} ± 0.1	0.6^{a} ± 0.0	0.6^{a} ± 0.1	0.6^{a} ± 0.2
	18- 30	0.8^{a} ± 0.3	0.4^{a} ± 0.0	0.4^{a} ± 0.0	0.4^{a} ± 0.2
	30- 60	0.6^{a} ± 0.1	0.4^{a} ± 0.0	0.4^{a} ± 0.0	0.3^{a} ± 0.2
	60- 90	0.6^{a} ± 0.1	0.4^{a} ± 0.0	0.4^{a} ± 0.0	0.4^{a} ± 0.1
	90-120	0.6^{a} ± 0.1	0.4^{a} ± 0.0	0.4^{a} ± 0.0	0.4^{a} ± 0.2
K	0- 8	0.62^{a} ± 0.23	0.72^{a} ± 0.25	0.62^{a} ± 0.27	0.96^{a} ± 0.37
me/100g	8- 18	0.30^{a} ± 0.10	0.45^{a} ± 0.13	0.30^{a} ± 0.09	0.35^{a} ± 0.10
	18- 30	0.30^{a} ± 0.15	0.56^{a} ± 0.16	0.36^{a} ± 0.12	0.29^{a} ± 0.08
	30- 60	0.33^{a} ± 0.04	0.58^{a} ± 0.35	0.41^{a} ± 0.07	0.32^{a} ± 0.06
	60- 90	0.39^{a} ± 0.06	0.20^{a} ± 0.04	0.30^{a} ± 0.03	0.34^{a} ± 0.09
	90-120	0.43^{b} ± 0.05	0.14^{a} ± 0.01	0.31^{ab} ±0.02	0.36^{b} ± 0.11
NO_3-N	0- 8	7.2^{a} ± 5.2	4.2^{a} ± 1.3	9.1^{a} ±15.7	7.2^{a} ± 3.4
	8- 18	10.4^{a} ±15.0	1.5^{a} ± 0.4	0.9^{a} ± 0.9	6.1^{a} ± 3.3
ug/g	18- 30	23.4^{a} ±41.6	0.2^{a} ± 0.2	0.1^{a} ± 0.2	1.3^{a} ± 0.5
NH_4-N	0- 8	18.1^{a} ± 6.3	10.5^{a} ± 1.5	9.5^{a} ± 3.4	13.2^{a} ± 2.8
	8- 18	9.7^{a} ± 3.8	3.9^{a} ± 0.5	3.4^{a} ± 0.2	7.1^{a} ± 1.4
ug/g	18- 30	12.5^{a} ± 9.6	3.1^{a} ± 0.2	3.0^{a} ± 0.3	3.9^{a} ± 0.7
TKN	0- 8	1.19^{a} ± 0.68	0.24^{a} ± 0.03	0.19^{a} ± 0.03	0.54^{a} ± 0.13
%	8- 18	1.11^{a} ± 0.59	0.15^{a} ± 0.04	0.09^{a} ± 0.01	0.47^{a} ± 0.14
	18- 30	1.03^{a} ± 0.94	0.05^{a} ± 0.00	0.05^{a} ± 0.01	0.26^{a} ± 0.10
P	0- 8	8.5^{a} ± 6.2	47.8^{b} ± 8.1	7.8^{a} ± 2.9	8.1^{a} ± 9.8
ug/g	8- 18	5.5^{a} ± 6.2	29.0^{a} ±15.4	5.0^{a} ± 2.1	3.4^{a} ± 5.8
	18- 30	5.4^{a} ± 6.6	3.6^{a} ± 2.3	1.0^{a} ± 1.0	2.7^{a} ± 5.4
TS	0- 8	0.15^{a} ± 0.10	0.02^{a} ± 0.01	0.01^{a} ± 0.00	0.05^{a} ± 0.02
%	8- 18	0.14^{a} ± 0.10	0.01^{a} ± 0.01	<0.01^{a} ± 0.00	0.04^{a} ± 0.01
	18- 30	0.16^{a} ± 0.16	0.01^{a} ± 0.01	<0.01^{a} ± 0.00	0.02^{a} ± 0.01
	30- 60	<0.01^{a} ± 0.01	<0.01^{a} ± 0.00	<0.01^{a} ± 0.00	0.01^{a} ± 0.01
	60- 90	<0.01^{a} ± 0.00	<0.01^{a} ± 0.00	<0.01^{a} ± 0.00	0.01^{a} ± 0.01
	90-120	<0.01^{a} ± 0.00	<0.01^{a} ± 0.00	<0.01^{a} ± 0.00	0.01^{a} ± 0.01
$CaCO_3$ eq	0- 8	2.9^{a} ± 2.9	0.1^{a} ± 0.2	0.2^{a} ± 0.2	0.0^{a} ± 0.1
%	8- 18	2.2^{a} ± 2.1	0.0^{a} ± 0.0	0.0^{a} ± 0.0	0.0^{a} ± 0.0
	18- 30	5.0^{a} ± 7.6	0.0^{a} ± 0.0	0.1^{a} ± 0.2	0.0^{a} ± 0.0
	30- 60	8.4^{a} ± 8.7	0.9^{a} ± 0.9	5.0^{a} ± 7.4	1.5^{a} ± 3.0
	60- 90	5.1^{a} ± 5.8	12.4^{ab} ± 4.9	21.6^{b} ± 6.2	0.8^{a} ± 1.2
	90-120	4.1^{a} ± 6.2	28.3^{a} ± 9.0	26.8^{a} ±13.5	4.7^{a} ± 5.8
TC	0- 8	22.2^{a} ±13.2	3.3^{a} ± 0.5	2.6^{a} ± 0.6	5.4^{a} ± 1.1
%	8- 18	17.3^{a} ±11.4	2.2^{a} ± 0.8	1.3^{a} ± 0.1	4.4^{a} ± 1.2
	18- 30	20.9^{a} ±18.5	0.8^{a} ± 0.2	0.4^{a} ± 0.2	2.7^{a} ± 1.0
	30- 60	2.0^{a} ± 0.4	0.7^{a} ± 0.1	1.2^{a} ± 0.9	2.5^{a} ± 1.0
	60- 90	1.2^{a} ± 0.6	1.8^{a} ± 0.6	2.7^{a} ± 0.7	2.2^{a} ± 0.8
	90-120	0.8^{a} ± 0.8	3.7^{a} ± 1.1	4.1^{b} ± 0.2	2.3^{ab} ± 0.3

continued ...

Table 4. (Continued).

		A	B	C	D
Clay %	0- 8	organic	15.3^{a} ± 2.7	14.6^{a} ± 2.3	20.3^{a} ± 4.2
	8- 18	organic	21.5^{a} ± 4.8	16.1^{a} ± 3.3	20.9^{a} ± 6.6
	18- 30	organic	31.4^{a} ± 0.6	24.2^{a} ± 6.4	24.5^{a} ± 7.1
	30- 60	27.5^{a} ± 2.8	35.5^{a} ± 3.0	26.9^{a} ± 4.8	23.9^{a} ± 3.6
	60- 90	33.8^{a} ± 3.6	16.3^{a} ± 3.3	26.6^{a} ± 6.4	27.1^{a} ± 9.4
	90-120	32.3^{a} ± 8.1	23.6^{a} ± 1.8	37.0^{a} ± 5.0	29.5^{a} ± 8.3
Sand %	0- 8	organic	41.4^{a} ± 3.0	45.1^{a} ± 7.0	41.4^{a} ± 9.1
	8- 18	organic	35.1^{a} ± 2.1	45.6^{a} ± 3.3	40.8^{a} ± 11.8
	18- 30	organic	37.6^{a} ± 7.6	40.4^{a} ± 8.9	40.7^{a} ± 10.4
	30- 60	33.6^{a} ± 2.8	49.6^{a} ± 7.9	31.6^{a} ± 9.9	44.6^{a} ± 11.9
	60- 90	42.5^{ab} ±10.7	62.5^{b} ± 3.8	25.6^{a} ± 8.6	45.2^{ab} ±15.4
	90-120	42.6^{ab} ± 8.7	56.6^{b} ± 4.1	12.7^{a} ± 1.5	43.9^{b} ± 16.1
DTPA-extractable					
AL ug/g	0- 8	2.8^{a} ± 1.8	7.9^{a} ± 8.6	7.1^{a} ± 4.3	4.2^{a} ± 2.9
	8- 18	3.9^{a} ± 5.5	3.0^{a} ± 3.3	2.0^{a} ± 1.4	4.1^{a} ± 3.6
	18- 30	2.1^{a} ± 1.5	1.6^{a} ± 0.6	0.8^{a} ± 0.5	1.4^{a} ± 1.0
	30- 60	1.2^{a} ± 0.4	0.7^{a} ± 0.4	0.3^{a} ± 0.4	0.8^{a} ± 1.0
	60- 90	1.0^{a} ± 0.2	0.5^{a} ± 0.5	0.2^{a} ± 0.3	0.8^{a} ± 0.5
	90-120	1.1^{a} ± 0.2	0.5^{a} ± 0.5	0.2^{a} ± 0.3	0.4^{a} ± 0.5
Cu ug/g	0- 8	1.2^{ab} ± 0.3	0.4^{a} ± 0.1	0.4^{a} ± 0.1	1.6^{b} ± 0.6
	8- 18	1.2^{ab} ± 0.4	0.2^{a} ± 0.0	0.2^{a} ± 0.0	1.8^{b} ± 0.8
	18- 30	1.0^{a} ± 0.3	0.4^{a} ± 0.1	0.4^{a} ± 0.2	1.9^{a} ± 1.0
	30- 60	1.0^{a} ± 0.3	0.8^{a} ± 0.2	0.8^{a} ± 0.3	1.8^{a} ± 0.9
	60- 90	1.2^{ab} ± 0.4	0.6^{a} ± 0.1	1.0^{ab} ± 0.2	2.4^{b} ± 0.8
	90-120	1.3^{a} ± 0.6	0.6^{a} ± 0.2	1.0^{a} ± 0.2	2.5^{a} ± 1.0
Fe ug/g	0- 8	107^{a} ± 47	99^{a} ± 46	95^{a} ± 17	316^{b} ± 78
	8- 18	110^{ab} ± 79	71^{a} ± 19	61^{a} ± 6	259^{b} ± 71
	18- 30	83^{a} ± 67	64^{a} ± 13	56^{a} ± 17	142^{a} ± 36
	30- 60	69^{a} ± 49	56^{a} ± 4	54^{a} ± 23	97^{a} ± 13
	60- 90	39^{ab} ± 22	25^{a} ± 3	28^{a} ± 6	75^{b} ± 14
	90-120	32^{a} ± 11	20^{a} ± 4	22^{a} ± 2	51^{a} ± 18
Mn ug/g	0- 8	11.2^{a} ± 5.0	24.5^{a} ±13.3	30.2^{ab} ± 9.8	67.8^{b} ±17.5
	8- 18	6.8^{a} ± 3.3	9.4^{a} ± 2.5	12.7^{a} ± 2.1	43.0^{a} ±33.9
	18- 30	2.8^{a} ± 1.8	5.2^{a} ± 1.8	11.0^{a} ± 2.5	21.0^{a} ±18.2
	30- 60	1.4^{a} ± 1.4	6.7^{a} ± 1.3	10.0^{a} ± 4.7	16.4^{a} ±13.1
	60- 90	1.9^{a} ± 1.2	1.9^{a} ± 0.6	4.5^{a} ± 1.9	21.0^{a} ±13.8
	90-120	4.0^{a} ± 2.0	1.8^{a} ± 0.2	4.2^{a} ± 0.5	16.4^{a} ±11.6
Mo ug/g	0- 8	0.2^{a} ± 0.4	0.0^{a} ± 0.0	0.6^{a} ± 0.5	0.0^{a} ± 0.0
	8- 18	0.4^{a} ± 0.3	0.1^{a} ± 0.2	0.2^{a} ± 0.2	0.0^{a} ± 0.0
	18- 30	0.5^{a} ± 0.3	0.0^{a} ± 0.0	0.0^{a} ± 0.0	0.0^{a} ± 0.0
	30- 60	0.7^{a} ± 0.5	0.0^{a} ± 0.0	0.0^{a} ± 0.0	0.0^{a} ± 0.0
	60- 90	0.2^{a} ± 0.1	0.0^{a} ± 0.0	0.0^{a} ± 0.0	0.0^{a} ± 0.0
	90-120	0.2^{a} ± 0.2	0.0^{a} ± 0.0	0.0^{a} ± 0.0	0.0^{a} ± 0.0

continued ...

Table 4. (Concluded).

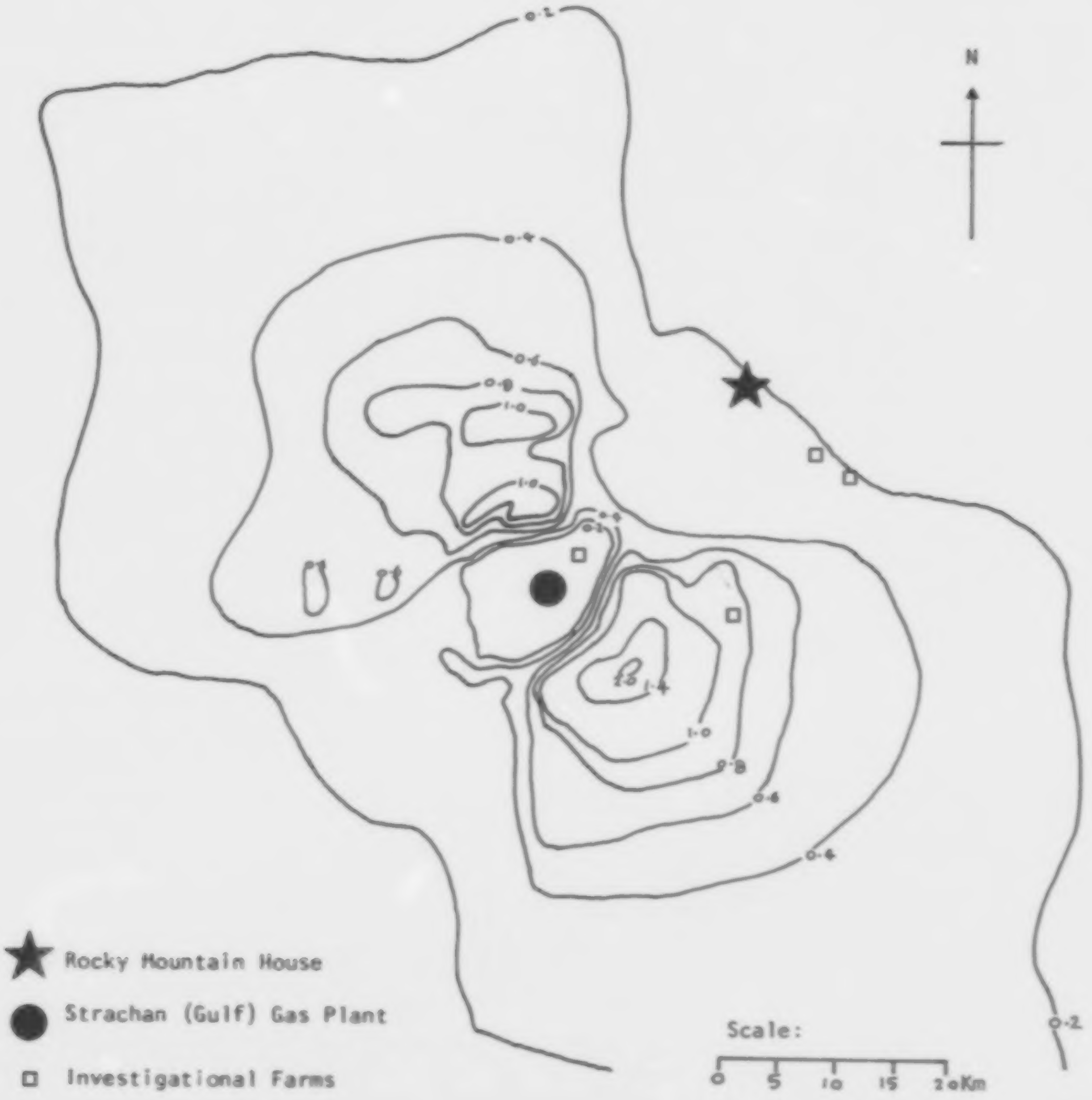
		A	B	C	D
Ni ug/g	0- 8	$1.5^{a} \pm 0.3$	$0.6^{a} \pm 0.1$	$0.5^{a} \pm 0.2$	$2.6^{a} \pm 1.6$
	8- 18	$1.5^{ab} \pm 0.3$	$0.4^{a} \pm 0.1$	$0.4^{a} \pm 0.1$	$3.1^{b} \pm 1.5$
	18- 30	$1.4^{a} \pm 0.6$	$0.6^{a} \pm 0.1$	$0.4^{a} \pm 0.2$	$3.0^{a} \pm 1.5$
	30- 60	$1.1^{ab} \pm 0.5$	$0.9^{ab} \pm 0.2$	$0.5^{a} \pm 0.0$	$2.4^{b} \pm 0.9$
	60- 90	$1.0^{a} \pm 0.5$	$0.4^{a} \pm 0.1$	$0.5^{a} \pm 0.2$	$2.7^{b} \pm 0.7$
	90-120	$0.9^{a} \pm 0.6$	$0.4^{a} \pm 0.1$	$0.4^{a} \pm 0.1$	$2.4^{a} \pm 1.3$
No. of samples (each sample from 3 subsamples)		5	4	5	5

[1] Means were compared using Scheffe multiple contrasts. Mean values followed by the same superscript letter indicates no significant difference between the means at $\alpha = 0.05$.

A small area was sampled on each of the cooperating farms. The soils within these areas are probably not very representative of the soils on each farm, but do represent a sampling of a range of soils found in the study area. Although these soils are genetically quite different, the measurements made are variable enough so that statistical significance related to soil class is often not expressed. Most of the soils have pH values above 5.5, the approximate minimum for general agricultural crop production. Water-soluble ion concentrations are low but in "acceptable" proportions. Sulphate concentrations are low enough to suggest sulphur deficiency at some sites. Soils sampled on farms B and C contained lime in the root zone, often within 30 to 60 cm of the soil surface. The soils are usually at least 80 per cent base saturated. Calcium, magnesium and potassium account for about 60-70, 10-20 and less than 3 per cent respectively, of the base saturation. Exchangeable potassium tends to be low and may be deficient for crop growth in some instances. Plant available nitrogen and phosphorus are variable and may be deficient at some sites. Ammonium nitrogen levels tend to be higher than nitrate nitrogen; this may indicated poor conversion of ammonium to nitrate. Levels of copper and zinc fall within ranges considered adequate for crop growth although some copper values are near deficient levels. Manganese and aluminium toxicities may be developing at some sites.

3.3 AIR

The first order estimates of sulphur deposition are plotted for the Strachan (Figure 1) and Ram River (Figure 2) gas plants. These indicate a maximum annual deposition rates of approximately 2 kg/h from each plant. Further work is necessary to merge these two estimates and to verify the accuracy of the estimates by measurements of ground impingement. The on-site air quality data will be collected for one year before interpretation of results.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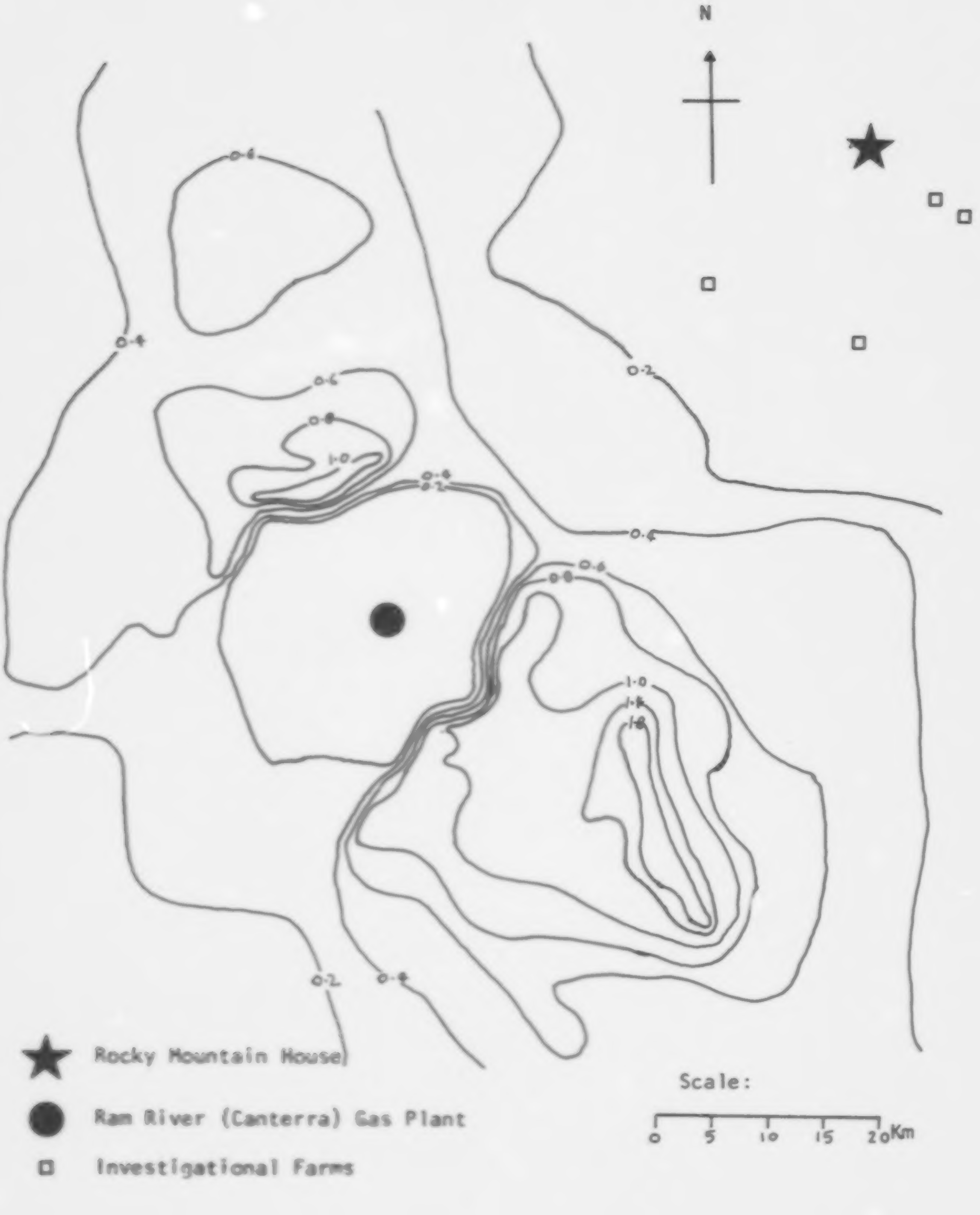
Rocky Mountain House
Strachan (Gulf) Gas Plant
Investigational Farms
Scale:
0
5
10
15
20 Km

Figure 1. Annual Sulphur Deposition (kg/hectare) for the Strachan (Gulf) Gas Plant; First Order Estimate.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★ Rocky Mountain House
● Ram River (Canterra) Gas Plant
□ Investigational Farms
Scale:
0 5 10 15 20 Km

Figure 2. Annual Sulphur Deposition (kg/hectare) for the Ram River (Canterra) Gas Plant; First Order Estimate.

3.4 BOVINE BLOOD

The results of the glutathione peroxidase enzyme assay are given in Table 5. In cattle this enzyme is 100 per cent seleno-dependent, thus the enzyme activity is proportional to the amount of selenium in the blood and is an indicator of the biological selenium status. There was no significant difference in enzyme activity levels in blood from cattle on farm D and from cattle randomly selected in another area of the province not associated with gas plant emissions.

Table 5. Enzyme activity of glutathione peroxidase in blood from two areas in Alberta.

Farm	No. of samples	Mean Activity/gm Haemoglobin ±.S.D.
D	20	50.2±13.3
Outside of area	25	40.8±17.7

3.5 CONCLUSION

The perceived problem of the possible effects of environmental sulphur on farm animals has two components:

1. The indirect effects of sulphur and sulphur-selenium antagonism as expressed in soils and plants;
2. The direct effects on animals of long term exposure to low levels of sulphur-containing emissions.

The results of this pilot study in the Rocky Mountain House area indicate that both soils and the crops grown on those soils tend to be low or deficient in a number of animal nutrients, including sulphur and selenium. In addition, the pilot study will facilitate future research into the efects of environmental sulphur.

The cooperation of the four farmers and their familes, Drs. B. Bourne and M. Kostuch, and Mr. T. Seabourne is greatly appreciated.

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THE EFFECT OF SO_2 ON FOOD QUALITY FOR WILD HERBIVORES

by

George G. Shaw[1] and Lewis Cocks[1]

ABSTRACT

During 1980 and 1981 potted plants of western serviceberry (*Amelanchier alnifolia*), willow (*Salix bebbiana* Sarg and *S. Alba vitellina* J. Stokes) and red fescue grass (*Festuca rubra* L.) were placed in the ground downwind of known SO_2 emission sources in Alberta to measure the effects of excessive SO_2 on element concentrations in plant tissues. In particular, depression of foliar selenium concentration has been caused by excessive SO_4, SO_2 and S under experimental conditions of higher S than may be found under field conditions. Experimental reductions of foliar selenium by SO_2 occurred at foliar selenium concentrations above 0.1 ppm, the threshold for development of selenium deficiency conditions in some ungulates. By monitoring concentrations of selenium and S in the plants and S in sulphation plates at each site for 2 or 3 years, we will determine if SO_2-related selenium depression in plants of nutritional significance to wild herbivores occurs under field conditions.

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1. INTRODUCTION

Concern for the effect of excessive atmospheric SO_2 on food quality for wild herbivores has several bases. In the first place Hurd-Karrer (1935, 1937), Davies and Watkinson (1966), Gissel-Nielsen (1973) and Shaw (1981) have shown that excessive S, SO_4 or SO_2 are associated with reductions of the essential element, selenium, in several plant species. Stadtman (1977), Harr (1978) and Hoekstra (1974), among others, have explained the essentiality of selenium to warm-blooded vertebrates, particularly large herbivores. When dietary concentrations of selenium remain below the range of 0.03 to 0.1 ppm, conditions such as white muscle disease, growth inefficiency and high calf mortality develop in domestic livestock. Symptoms of selenium and/or Vitamin E deficiencies have been reported also in several wild vertebrates (MacDonald et al. 1976) and Zoo herbivores (NZP 1971).

SO_2 concentrations of 0.01 to 0.5 ppm are frequently encountered downwind of fossil fuel combustion sites. Persistent exposure to these low SO_2 concentrations may depress foliar selenium just as low as SO_4 fertilization was shown to do in red clover (Gissel-Nielsen 1973). Such depressions even occurred for initial foliar concentrations of 0.1 ppm selenium and lower. Moreover, excessive foliar SO_4 results from SO_2 exposure (Addison and Baker 1979, Case and Krouse 1979, Shaw 1981) and excessive dietary SO_4 has been shown to increase excretion rates of selenium from rats (Ganther and Bauman 1962) and may induce deficiencies of other elements such as Cu (Suttle 1976, Flynn et al. 1979).

As a result of these studies and others on acid rain SO_4 effects (Moser et al. 1980, Lechowicz 1981), the Canadian Wildlife Service is conducting research to bridge the gap between results of highly controlled experiments and the field situation. The field project reported here will determine if depression of selenium concentration and changes in other element concentrations of leaves occur in potted plants growing in the vicinity of sour gas and oilsands processing plants during a three-year period.

Both these major industries of Western Canada will continue to emit gaseous and aerosol sulphur to the atmosphere during the next

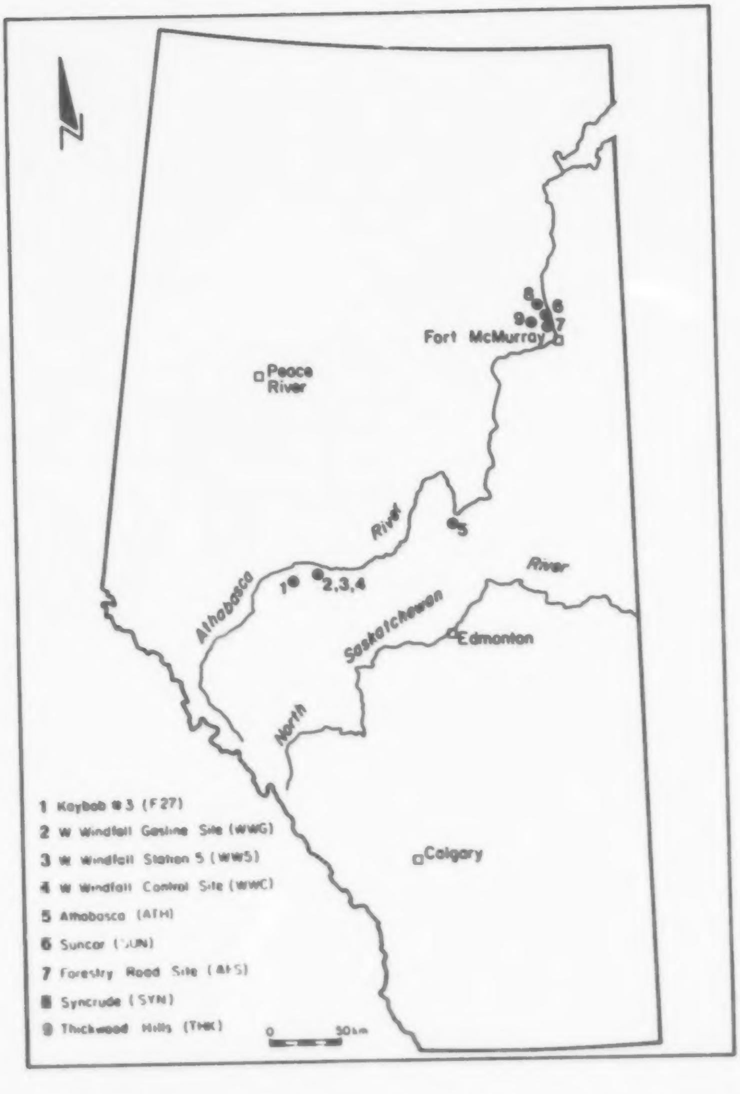
Fort McMurray
Peace River
Athabasca River
North Saskatchewan River
Edmonton
Calgary
1
2,3,4
5
6
7
8
9
1 Kaybob # 3 (F27)
2 W Windfall Gasline Site (WWG)
3 W Windfall Station 5 (WW5)
4 W Windfall Control Site (WWC)
5 Athabasca (ATH)
6 Suncor (SUN)
7 Forestry Road Site (AFS)
8 Syncrude (SYN)
9 Thickwood Hills (THK)
0
50km

Figure 1. Exposure sites of potted plants to ambient concentrations of SO_2 downwind of sourgas and oilsand processing industries in Alberta.

two decades. These emissions will be deposited regionally as slightly acidified rain (Rudbec 1981), aerosols or as dry ammonia sulphate particulates. Our concern is whether or not these depositions will be sufficient to cause significant widespread change in food quality for wild herbivores. The generality of this concern is not premature because widespread but slight selenium reductions in livestock forages of Denmark between 1964 and 1973 have been documented (Gissel-Nielsen 1975). Acidified rain increased substantially over Denmark during that time period. Moreover, selenium concentrations of less than 0.1 ppm have been found in samples of several plant species fed upon by wild herbivores in Northern Alberta (CWS unpublished data).

2. METHODS

2.1 FIELD SITES AND SO_2 EXPOSURE

Initial placement of potted plants at 9 field sites (Figure 1) occurred in two consecutive field seasons instead of one. This resulted in a few important differences in methods, which also extend to the presentation of results in this report and to project activities during the next two field seasons.

Field sites were established during 1 to 14 July 1980, 1.5 km southeast of the Amoco gas processing plant at West Windfall (WWG), 3.0 and 6.5 km southwest of the Suncor oilsands plant (SUN and AFS, respectively), and 10 km southwest of Athabasca (ATH). WWG and SUN sites were chosen as high SO_2 impingement locations because SO_2 can frequently be smelled there, indicating concentrations of 0.5 to 0.7 ppm (Sunshine 1969, p 709). Since there was no known SO_2 source upwind of the ATH site, concentrations of the gas were expected to be low.

Ten similar sized plants of Northline serviceberry (***Amelanchier alnifolia***) and golden willow (*Salix alba vitellina* J. Stokes), potted singly in 22 L, 1:1:1 mixtures of peatmoss, vermiculite and silica sand (PVS soil), were placed in the ground to a depth which left 10 cm of the pots exposed. All pots had a series of drainage holes at their bases. Each site was fenced to exclude ungulate and lagomorph browsing.

During 10 to 30 June 1981, five similar sites were established: (1) 0.6 km east of the Syncrude oilsands plant (SYN); (2) 28 km southwest of Syncrude, about 80 m north of the fire tower road to Thickwood Hills (THK); (3) 6 km southeast of Chevron's Kaybob #3 gas processing plant (F27); (4) 4 km east of the West Windfall plant (WW5); and (5) 11.3 km north of the same plant (WWC). The 1981 sites were chosen after careful study of data from 40 sulphation stations operated by each of the industries according to provincial regulations. Sites F27 and WW5 were within 100 m of industrial sulphation stations; Chevron and Amoco, respectively. WWC and THK sites were chosen as control sites having low concentrations of SO_2.

Sixteen pots of Northline serviceberry and 8 pots of red fescue grass (*Festuca rubra* L.) were established at each of these sites. Half of the pots of serviceberry had soils amended with iron III selenite to a concentration of 0.1 ppm selenium. Six pots each of beaked willow (*Salix bebbiana* Sarg.) with unamended soil were added to WWG, WW5 and WWC sites in early August 1981.

Average monthly sulphation has been measured at all nine sites since June 1981 using Huey plates similar to those of Addison and Baker (1979). Three Huey PbO_2 sulphate plates 1 m above the groune and 2 m apart were exposed at each site. Analysis for mg SO_3/100 cm^2/day on sulphation plates was determined by Norwest Feeds Research Ltd. using carbonate extraction (Alberta Environment 1981) and methyl thymol blue soluble sulphate determination (Technicon 1972).

2.2 PLANTS AND SOIL

During April 1980 several hundred terminal shoots from one golden willow tree were rooted in vermiculite using Rootone^R. As many terminal shoots cut from beaked willow trees in uplant mixed-wood forest near Gregoire Lake, Alberta were similarly treated. Rooting and subsequent establishment of these native willows was difficult and required the whole growing season of 1980. As beaked willow is difficult to identify, the individual potted plants were retained at the Northern Forest Research Station until 1981 to insure that at least morphologically similar willow plants were moved to field sites in 1981.

Serviceberry of the Northline variety, originating from the Beverlodge Nursery in Alberta were purchased locally and established successfully at field sites in 1980. In 1981 similar stock obtained directly from the nursery appeared to die during establishment in 22 L pots. Accordingly, somewhat smaller plants of the Hilson variety of serviceberry provided by the Oliver Tree Nursery of Alberta Agriculture were planted alongside the Northline plants in each pot. Whichever variety is alive in 1982 will be retained and plants of the other variety removed.

Red fescue grass grew better in the PVS soil mixture than several other grasses. Accordingly, 1 gm of red fescue seed was distributed evenly over the soil surface in pots which were subsequently moved to field sites after the grass was several cm high.

Prior to transfer to field sites in 1980 all potted plants were similarly fertilized with a 5% standard concentration of Hoagland's #2 solution (Hoagland and Arnon 1950). In 1981 all pots were fertilized once, prior to transfer, in accordance with recommendations from PVS soil tests by the soil and feed testing laboratory of Alberta Agriculture.

In 1980, all PVS soils was hand-mixed in 220 L quantities and then evenly distributed into 22 litre pots which were randomized for planting of root stock. In 1981, all PVS soils were mixed in a large mechanical soil mixer at the Oliver Tree Nursery.

Iron III selenite which is very insoluble was incorporated into batches of dry PVS soil within the mechanical mixer in the following way. The amount of iron III selenite required to produce 0.1 ppm selenium-PVS soil was first blended into 3 L of dry premixed PVS soil using a large Waring blender. The resulting powdered concentrate was slowly added to the large mixer batch of dry PVS soil during the 10 min. of dry mixing before adding water. Pots of PVS soil were randomized for planting and seeding.

2.3 FOLIAR SAMPLING AND ANALYSIS

In 1980, 4 cm^2 mesh net bags were placed over the top 10 leaves of each potted plant in late August to retain the leaves if leaf drop was unexpectedly early. Composite samples of fallen and attached leaves for serviceberry were made at each site. These samples were dried and ground to pass a 40-mesh sieve. Foliar selenium analysis using "DAN" reagent and fluorometry (Levesque and Vendette 1971) was done by the Kananaskis Center for Environmental Research.

On September 25, 1981, red fescue was clipped in all pots at each site. Each of the 5 composite samples was washed in distilled water to remove superficial soil. Composite, site-specific samples of serviceberry and willow were collected on September 8, 1980 from the top 10 leaves on each plant. Composite samples of Hilson serviceberry were collected where possible at SYN and THK sites on September 24. All leaves were surface brushed to remove loose material and then divided into green and necrotic tissues for each species. All samples were dried and ground to pass a 40-mesh sieve.

Foliar selenium concentration was determined by Barringer Magenta Ltd. using the hydride generation method (Environment Canada 1979). This laboratory also determined foliar concentrations of Al, Ag, Ba, Be, Cd, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sr, Th, Ti,V, Zn, and Zr by inductively coupled plasma emission spectormetry (ICP). Foliar sulphur concentration was determined by Norwest Feed Research Ltd. using infrared detection of SO_2 during combustion of samples in a Leco furnace.

Standard statistical procedures were used to determine if plant heights and sulphation rates differed between sites and to describe several attributes of the foliar elemental data.

3. RESULTS

No differences in average plant height of Northline serviceberry or golden willow were detected among sites (Table 1). The average height of willow at AFS was shorter because terminal shoots were browsed or cut by an unknown animal during the winter of 1980 and the summer of 1981.

Table 1. Average height (cm) of potted Northline serviceberry and golden willow grown at 4 field sites.

	Site			
	ATH	WWG	AFS	SUN
Northline serviceberry	95	93	82	93
golden willow	176	110	35	122

Sulphation data (Table 2) were corrected for method accuracy which was 92% of prepared standards. Precision of analysis was consistently 5% or better. Average percent variation among the three sulphation stations at each site was 8.5%. Application of analysis of variance and Duncan's multiple range test ($p = 0.05$) to monthly sulphation rates from June 25 to September 9 indicated that only the WWC site significantly different from any other site for sulphation (Table 3).

Analytical precision for percent sulphur in composite foliar samples (Table 3) was 5%. Percent sulphur concentration in foliage was not correlated with site sulphation rate for any of the three species.

Average concentration of foliar selenium in Northline serviceberry and golden willow in late September 1980 was similar for fallen and attached leaves (Table 4.) If site-specific sulphation rates of 1980 were similar to those of 1981 (Table 3) the foliar selenium concentrations were not correlated with sulphur exposure across sites. Accuracy of the flurometric method was high and precision was 15% among duplicate determinations.

Average concentrations of foliar selenium in red fescue, Northline serviceberry and golden willow were appreciably lower at the end of the 1981 field season (Table 5). However, these data derived by the hydride generation method are far less reliable than those of 1980 because of much lower accuracy a precision of 29% among replicate determinations.

Of the elements analyzed by ICP only Al, Ba, Ca, Cu, Fe, K, Mg, Mn, P, Sr, Ti, V, and Zn had average concentrations sufficiently above detection levels to analyze statistically (Table 5). Average

Table 2. Average sulphation (3 stations each) in mg $SO_3/100\ cm^2$/day at 9 field sites where potted plants were growing (1981-82). Average standard deviation was 0.003 ± 0.001.

Site	June 25 July 20	July 20 Aug. 19	Aug. 19 Sept. 9	Sept. 9 Sept. 24	Sept. 24 Oct. 21	Oct. 21 Nov. 24	Nov. 24 Jan. 23	Jan. 23 Feb. 25
WWC	.002	.004	.008	.010	.006	.001	.022	.022
WW5	.029	.014	.051	.046	.020	.013	.039	.060
WWG	.048	.021	.042	.035	.032	.022	.017	.027
F27	.040	.040	.066	.055	.028	.023	.031	.049
ATH	.026	.022	.026	.057	.030	.016	.047	.082
THK	.051	.017	.040	.070	.024	.022	.035	.052
AFS	.051	.022	.040	.050	.047	.012	.025	.036
SYN	.046	.047	.044	.081	.032	.023	.056	.031
SUN	.029	.017	.086	.054	.038	.022	.053	.039
Average	.036	.023	.045	.051	.029	.017	.036	.044

Table 3. Average daily sulphation (June 25 - September 9) and % sulphur concentration in leaves of 3 plant species (September 9) at 9 sites in 1981.

Location	Sulphation $mgSO_3/100\ cm^2/day$	red fescue	Northline serviceberry	golden willow
WWC	0.005	0.110		
WW5	0.031	0.124		
WWG	0.037		0.132	0.534
F27	0.048	0.105		
ATH	0.025		0.204	0.967
THK	0.036	0.186		
AFS	0.038		0.109	0.530
SYN	0.044	0.175		
SUN	0.044		0.151	0.429

Table 4. Average concentration of selenium (ppm) in Northline serviceberry and golden willow leaves at 4 locations in late September 1980.

	Serviceberry	Willow	
	Fallen	Fallen	Attached
ATH	0.61	0.37	0.34
WWG	0.51	0.30	0.47
AFS	0.14	0.42	0.44
SUN	0.25	0.47	0.15
Average	0.38	0.39	0.35

concentrations of Al, Fe, K, and Ti in red fescue were significantly greater than those of leaves from both serviceberry varieties and golden willow combined ($p = 0.05$). The reverse was true for Ca, Mg, Mn, and Sr concentrations in leaves.

A few other elements also differed between pairs of species. Foliar concentrations of Cu and Ni were greater for red fescue than for Hilson serviceberry at the only two sites where both were located. Concentrations of Fe, Ti, and Zn were greater in Northline than in Hilson serviceberry. Finally, concentration of Mn was significantly lower, and that of Zn higher, in golden willow compared to Northline serviceberry.

ICP data (Table 5) are single estimates for each site, hence no analysis of variance between sites was possible. No correlations of these element concentrations with SO_2 exposure (Table 3) were attempted because of an insufficient quantity of data.

Several paired samples of green and necrotic foliar tissue of Northline serviceberry were compared for all ICP-determined elements. Foliar concentrations of Ca and Mg were significantly higher in necrotic tissues than in green tissues on September 24 whereas the reverse was true for P. No other elemental differences in concentration were found.

Analytical precision for ICP analysis was good ($\leq 10\%$) for Al, Ca, K, Mg, Mn, P, and Sr; fair for Ba, Cu, Ti, and Zn, and poor for all other elements (Table 6). There was no difference between the average precision for orchard leaf replicates prepared by the contractor and those of other plant samples which were not identified for the contractor.

4. DISCUSSION

Although the results presented here are preliminary relative to the experimental objective, they should be of value as baseline data. Foliar changes in elemental concentrations in association with low SO_2 exposure were not expected to be evident in the first year of a 3 year field project.

Table 5. Concentrations of 14 elements (ppm) in foliar tissues of 4 species at several sites in 1981.

Species/Location	AL	BA	CA	CU	FE	K	MG	MN	P	SE (PPB)	SR	TI	V	ZN
Creeping red fescue[1]														
WWC	449	105	3554	4.57	488	26678	1644	274	1820	8.5	6.74	16.1	0.78	31
WW5	243	98	2757	4.44	491	30078	1456	290	2185	3.5	6.06	7.13	0.61	29
F27	313	99	3037	5.62	411	32078	1596	254	1705	8.5	6.35	16.3	1.0	26
THK	258	77	4547	3.48	251	28678	2066	208	1535	6.5	10.5	14.9	0.61	30
SYN	240	96	4047	3.29	310	26778	1936	228	1575	3.5	8.34	11.4	1.0	30
Average	356	99	3575	4.39	427	28040	1704	259	1785	6.1	7.3	14.2	0.80	30
Northline serviceberry[1]														
ATH	56	166	13487	4.43	102	9178	3156	1519	2585	51	33.1	1.56	0.20	38
WWG	23	22	5627	1.14	47	15478	2486	743	1295	9	9.4	0.24	0.25	13
AFS	65	62	9327	2.09	118	12578	3456	1099	1275	9	16.6	2.34	1.45	22
SUN	178	117	11187	1.03	147	7108	3886	1479	1585	1	22.5	3.65	1.38	20
Average	80	92	9907	2.17	104	11085	3246	1210	1685		20.4	1.95	0.82	23
Hilson serviceberry[2]														
THK	93	153	11687	1.34	233	10578	3806	1849	2445		27.8	4.57	0.20	67
SYN	151	91	9777	1.50	226	12378	3136	626	1815		24.2	5.35	0.57	45
SYN	131	91	9557	1.13	226	12378	3126	607	1725		23.9	4.91	0.42	45
Average	125	112	10340	1.32	229	11778	3356	1028	1995		25.3	4.90	0.42	52
Golden willow[1]														
ATH	38	11	10587	6.48	69	16778	5176	78	2025	29	30.9	0.94	0.0	60
WWG	47	35	11587	2.49	55	15878	3746	646	2015	9	16.7	1.08	0.0	81
AFS	118	76	15687	7.35	149	15278	5086	1079	2365	15	23.0	5.11	0.73	167
SUN	447	51	12487	16.28	221	13178	5046	749	1745	29	21.7	9.9	3.89	76
Average	162	43	12587	8.15	124	15278	4764	638	2038		23.1	4.3	1.12	96
Beaked willow[1]														
WWG	304	133	21687	4.68	291	7018	4566	187	1945	65	66.2	9.8	0.42	346

[1] collected September 8, 1981

[2] collected September 24, 1981

Given the similarity of sulphation rates at most sites (Table 3), two more sites will be established in 1982. One site will be comparable to WWC and the other site will be several times higher in sulphation rate than that of site F27. Serviceberry of whichever variety survives at 1981 sites and red fescue grass will be located at the new sites.

Different microclimates and leaf surface deposition of fine soil particulates may account for foliar differences in elemental concentrations between sites. However, growth rates have not differed between sites (Table 1) so different temperature and moisture regimes at the sites may not contribute to differences in foliar concentration of elements. Such differences (Table 5) may still reflect site-specific, leaf surface soil deposition as well as physiologically determined concentrations because the efficiency of leaf surface cleaning by washing or brushing is unknown. Accordingly, some monitoring of fine soil deposition on leaf surface analogues will be done in 1982.

One result (Table 5) worthy of additional comment is the grass-shrub difference in foliar concentrations of elements. Al, Fe, K, and Ti were greater in grass than in shrub leaves, whereas Ca, Mg, Mn, and Sr were greater in the latter than in the former plant foliage. These differences are consistent with grass versus shrub foliar data reported elsewhere for Fe, Ca, Mg, and Mn (Scotter and Miltmore 1972, Scotter 1972, Kubota et al. 1970, Doyle et al. 1973).

In conclusion, baseline data on foliar elemental concentrations for 3 species of vegetation receiving differential SO_2 exposure under field conditions have been established. Identification of analytical and a few other experimental design difficulties can be corrected in 1982. This project has received considerable and appreciated assistance from the Oliver Tree Nursery and Soil and Feed Testing Laboratory of Alberta Agriculture, and from personnel of the Air Pollution Control Division of Alberta Environment, of Alberta Forest Service and of Syncrude, Suncor, Chevron, and Amoco industries. Userful advice has also been given by Canadian Forestry Service scientists involved in SO_2 research at the Northern Forestry Research Station.

Table 6. Analytical precision of inductively-coupled plasma emission spectometry for concentrations of 17 elements in 5 different plant.

Plant tissue number of replicates		Al	Ba	Ca	Co	Cr	Cu	Fe	K	Mg	Mn	Mo	Ni	P	Sr	Ti	V	Zn
orchard leaves	$\bar{x}$	242	30	20053	-	2.2	11	281	13261	5169	83	2.2	1.7	1923	26	8.4	0.5	25
n=6	CV(%)	4.3	3.3	4.4	-	16	6.4	6.7	2.4	2.6	5.4	100	17	6.3	9.5	18	35	9.5
red fescue	$\bar{x}$	449	105	3554	-	1	4.6	488	26678	1644	274	-	1.4	1820	6.7	16	0.8	31
n=4	CV(%)	12	2	0.5	-	52	7.2	37	1.0	2.0	1.3	-	43	4.4	9.7	15	23	5.3
red fescue	$\bar{x}$	262	74	4202	5.0	2.4	3.3	219	29203	2206	328	13	4.3	1575	10	18	0.9	34
n=4	CV(%)	11	58	6.6	62	21	16	68	2.6	2.3	8.8	64	66	6.5	3.7	5.4	20	19
serviceberry	$\bar{x}$	141	91	9667	-	0.6	1.3	226	12378	3131	617	5.0	0.8	1770	24	5.1	0.5	45
n=2	CV(%)	10	0	1.6	-	83	20	0	0	0.2	2.2	100	35	3.6	0.9	6.1	21	0.8
serviceberry	$\bar{x}$	121	95	10687	0.3	0.3	3.1	249	10728	2951	2224	1	2.7	2435	18	4.3	0.1	104
n=2	CV(%)	1.8	3.9	6.6	377	57	9.1	7.9	4.6	6.5	8.6	100	11	9.9	0.8	6.8	106	25
Average	CV(%)	7.8	13	3.9	215	46	12	24	2.1	2.7	5.3	91	34	6.1	4.9	10	41	12

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SULPHUR AND OTHER MINERAL CONCENTRATIONS IN FEEDSTUFFS FED TO LIVESTOCK IN VARIOUS REGIONS OF ALBERTA

R. WESTRA[1]

ABSTRACT

Excess sulphur deposited in the soil may adversely affect the concentrations of certain micro-minerals in plants that are required by livestock. This paper presents data on the levels of sulphur, copper, selenium, manganese, and a number of other macro and micro elements found in Alberta feedstuffs. Field and laboratory investigations of livestock production problems are discussed in relation to the mineral concentrations of feedstuffs being fed to the problem herds. Investigations were made in various regions of Alberta and included areas where sulphur emissions were blamed as contributing to the livestock problems. It was observed that where sulphur emissions were blamed as the major cause of the problem, sulphur in the feedstuffs fed to the animals was not excessive; on the contrary, it was often marginal to deficient for meeting the minimum dietary requirements. The effect of sulphur on selenium and copper concentrations in feedstuffs and their interaction in ruminant digestion are discussed in relation to what was observed in the field.

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1. INTRODUCTION

The rate of acid-emission deposition in Alberta is of concern to agriculture because of the danger of increasing the acidity and total sulphur content of soils. Changes in pH and sulphur content in the soil alters the types of crops grown, the trace mineral uptake and concentrations in forages (Gissel-Nielsen 1973; Meiwes et al. 1980; Williams 1980; Underwood 1980, p. 12). At several locations in Alberta large amounts of sulphur-containing emissions from several sour gas plants have been blamed for the selenium deficiency found in feeds fed to livestock. Selenium is a necessary nutrient for the prevention of white muscle disease in calves and paralytic myoglobinuria in yearlings. It is one of several nutrients for the prevention of calf pneumonia, unthriftiness and poor growth in growing cattle, retained placenta and infertility in cows (Rickaby 1980). In sheep, a selenium deficiency leads to white muscle disease in growing animals, infertility, and unthriftiness and poor growth (MacDonald et al. 1976; Rickaby 1980).

Samples of feedstuffs were taken from farms in Alberta and submitted to the Agricultural Soil and Feed Testing Laboratory for macro and micro mineral analyses. Farms near 3 sour gas plants (SGP) were investigated, and forage and grain samples also were obtained and analyzed for macro and micro minerals. These results were then compared with those of other similar analyses of feedstuffs obtained throughout Alberta (A).

2. METHODS AND MATERIALS

Feedstuff samples were collected between October 1979 and July 1981 by various methods for submission to the laboratory for chemical analyses. The method used for collecting samples from stored feedstuffs on farms near SGP was by core sampling several bales of hay from each field and then the samples within each field were combined to represent one sample. Pasture samples were randomly selected and obtained by clipping one square meter blocks 1-2 cm from the surface of the ground. Grain samples were taken by grab method from several locations to the storage bin.

One hundred and thirty-four feedstuffs were collected from 14 farms situated downwind 2 to 20 km from a SGP. The farms were selected at the request of the producer because the farmer felt that some connection existed between the health of their animals and the assumed SGP emissions. Four of the farms were located in soil zone 5, two farms in soil zone 6, an eight farms were located in soil zone 8 (Figure 1). The SGP associated with the farms investigated were Amoco near Crossfield, Esso near Joffre, and Gulf near Rocky Mountain House. Feedstuffs received from A and analyzed for a variety of macro and micro minerals consisted of over 780 samples in total. There were very few of no feedstuffs obtained from farms in soil zones 3, 4, and 5.

Protein and phosphorus concentrations were determined in the feedstuffs using a Technicon Auto Analyzer and using standard methods (Association of Official Agricultural Chemists 1975). Sulphur, magnesium, sodium, calcium, potassium, copper, manganese, zinc, and iron were prepared by the wet ash method (Blanchar et al 1065) and except for sulphur the elements were determined by a Perkin-Elmer atomic absorption spectrophotometer (Perkin-Elmer Co. 1964). Sulphur content was determined by the method described by Johnson and Nishita (1952) and modified by Carson et al. (1972). Samples for selenium analyses were prepared and determined by the fluorometric method (Levesque and Vendette 1971). Samples for molybdenum analyses were prepared by the dry ash method (Gorsuch 1959), and determined using an argon spectrophotometer (Jones 1981).

3. RESULTS AND DISCUSSIONS

The means of the mineral and crude protein concentrations in stored feedstuffs submitted from farms near SGP were similar in most cases to those from farms throughout Alberta (A) as shown in Table 1. The means for P and Ca tended to be higher in the cereal hays near SGP

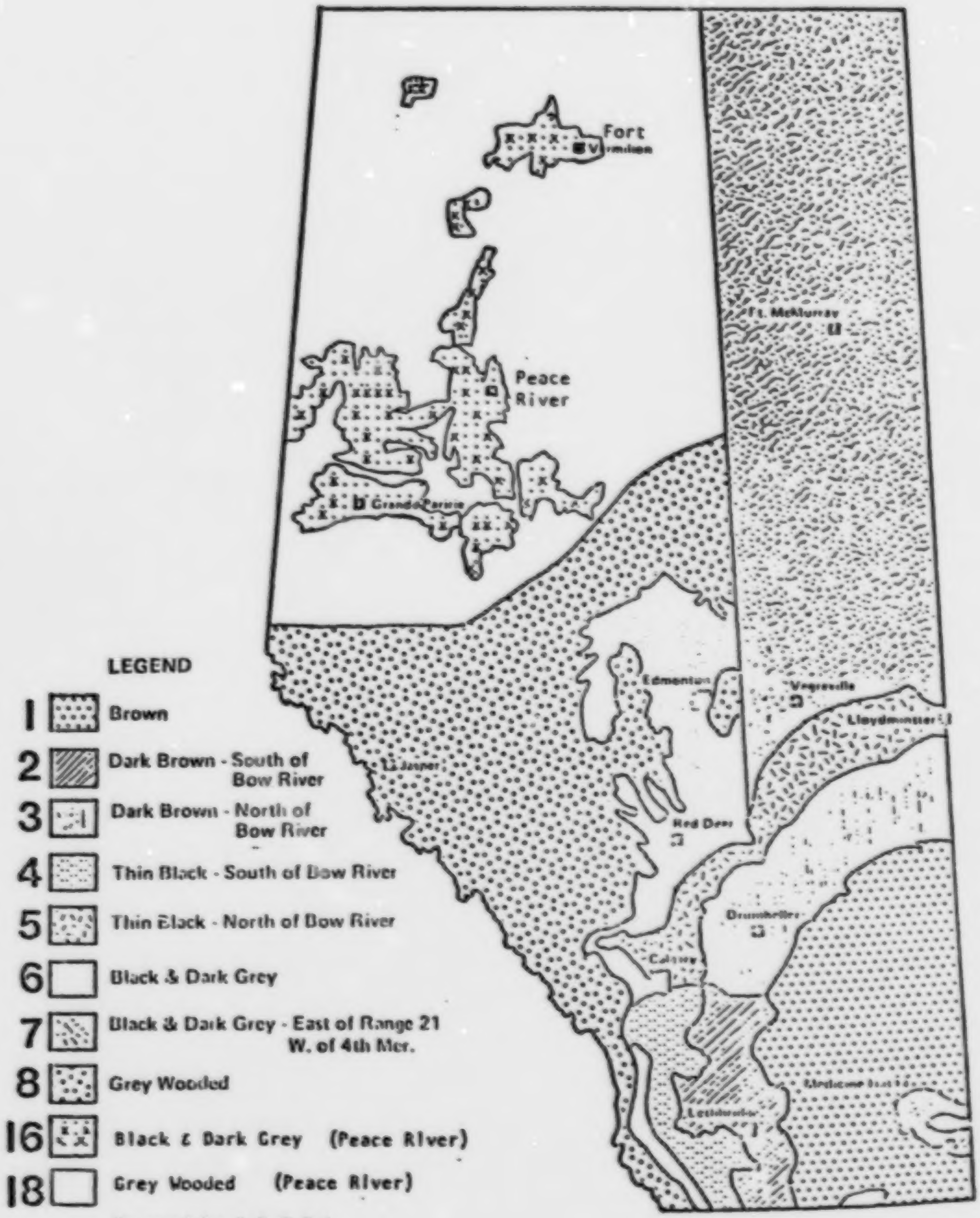
Fort Vermilion
Peace River
Grande Prairie
Ft. McMurray
Edmonton
Vegreville
Lloydminster
Jasper
Red Deer
Drumheller
Calgary
Lethbridge
Medicine Hat
LEGEND
1 Brown
2 Dark Brown - South of Bow River
3 Dark Brown - North of Bow River
4 Thin Black - South of Bow River
5 Thin Black - North of Bow River
6 Black & Dark Grey
7 Black & Dark Grey - East of Range 21 W. of 4th Mer.
8 Grey Wooded
16 Black & Dark Grey (Peace River)
18 Grey Wooded (Peace River)
As used by A.S.F.T.L.

Figure 1. Soil zones of Alberta subdivided for feed and soil test areas.

than in A. Aluminum and Fe were much lower in all the stored feedstuffs near SGP than in A. The means for Cy and Zn were lower in the roughage feedstuffs and the Se was higher in the grass-legume hays than those reported by Redshaw et al. (1978) and Horton and McElroy (1977). Many of the mean mineral values may reflect a differential selection of various feeds from farms where problems existed as a result of trace mineral deficiencies. A detailed breakdown by region of trace mineral average values in Alberta feedstuffs has been reported by Weisenburger (1981).

The pasture samples tended to have higher concentration means for S, Cu, Zn, Mo, Al, and Fe and lower concentration means for Se than any of the stored feedstuffs. The mineral concentrations of the pasture samples were higher than those harvested near Barrhead (Weisenburger 1981), and closer to meeting the minimum requirements of ruminants. Higher protein content in feeds apparently increases the availability of selenium (Byers and Moxon 1980) but reduces copper availability (Ivan and Veira 1981).

This may explain why copper deficiency symptoms are often observed when cattle are transferred from winter feeds to spring pastures. It was also suggested that higher sulphate content in pasture grasses may decrease the availability of Cu and Se in the digestion process (Hidiroglou 1980a, 1980b; Smart et al. 1981), but more important, this problem may be further aggravated primarily by the low concentrations of Cu and Se in pasture samples as shown in Table 1 and 2.

Lower than normal tonus activity of the uterus and slower than normal return to estrus after calving observed by some veterinarians (and discounted by others) in areas of Alberta where copper and zinc are deficient, may be directly related to each other. Animals on some farms, identified in this study, were diagnosed copper deficient and a positive response to copper therapy in calf growth was observed. It is known that animals fed zind deficient diets have slower rates of wound healing (Hidiroglou 1980a, 1980b) but animals deficient in both copper and zinc will also exhibit a reduced integrity of the epithilial tissues (Rucker and Murray 1978). Proteins such as collagen and elastin (and keratin in hair and hoof nails), are

Table 1. Means and standard deviations of protein and macro and micro mineral concentrations (dry matter basis) of feedstuffs grown throughout Alberta (A) and feedstuffs grown in areas near sour gas plants (SGP) (October 1979 to July 1981).

Feedstuff	Area Grown	Crude Protein	Macrominerals						Microminerals						
			Ca	P	Mg	K	Na	S	Se	Cu	Mn	Zn	Mo	Fe	Al
			%						ppm						
Cereal Roughages	A	9.3 (1.7)	0.33 (0.15)	0.21 (0.05)	0.158 (0.041)	1.85 (0.85)	0.187 (0.167)	0.149 (0.069)	0.187 (0.167)	4.7 (1.9)	39.5 (15.9)	20.5 (6.8)	0.562 (0.333)	726 (77)	957 (2419)
	SGP	10.3 (2.2)	0.34 (0.11)	0.25 (0.03)	0.182 (0.060)	1.61 (0.72)	0.070 (0.097)	0.153 (0.027)	0.220 (0.223)	4.8 (2.2)	41.3 (21.9)	23.3 (6.0)	0.810 (0.650)	175 (189)	81 (61)
Straws	A	4.4 (1.3)	0.31 (0.23)	0.10 (0.05)	0.120 (0.046)	1.55 (0.52)	0.247 (0.160)	0.135 (0.050)	0.308 (0.273)	3.6 (2.0)	31.9 (23.3)	13.3 (6.8)	0.720 (0.491)	113 (52)	91 (48)
	SGP	5.1 (1.5)	0.27 (0.07)	0.09 (0.04)	0.11 (0.05)	1.46 (0.16)	0.333 (0.280)	0.143 (0.260)	0.176 (0.113)	3.5 (1.3)	25.3 (8.6)	13.2 (7.7)	0.71 (0.45)	125 (102)	96 (30)
Grains	A	12.0 (1.9)	0.08 (0.03)	0.37 (0.05)	0.139 (0.016)	0.51 (0.10)	0.018 (0.016)	0.100 (0.019)	0.147 (0.205)	7.4 (12.8)	29.2 (14.7)	37.9 (14.9)	0.643 (0.443)	81 (47)	23 (20)
	SGP	12.7 (1.8)	0.07 (0.02)	0.38 (0.04)	0.142 (0.012)	0.57 (0.09)	0.009 (0.007)	0.093 (0.014)	0.110 (0.106)	5.7 (3.3)	32.6 (14.6)	33.2 (5.8)	0.500 (0.360)	58 (17)	21 (18)
Hays (Legume, Grass & Mixed)	A	12.9 (4.3)	1.05 (0.59)	0.19 (0.06)	0.215 (0.088)	1.78 (0.61)	0.059 (0.144)	0.154 (0.073)	0.256 (0.331)	6.8 (3.3)	52.8 (38.6)	23.6 (9.8)	1.32 (0.80)	237 (271)	542 (1240)
	SGP	13.9 (3.0)	0.96 (0.43)	0.19 (0.05)	0.204 (0.030)	1.97 (0.47)	0.019 (0.024)	0.131 (0.047)	0.193 (0.135)	7.0 (3.8)	50.1 (20.1)	21.4 (6.3)	1.25 (1.13)	107 (26)	84 (43)
Pastures	SGP	14.4 (5.3)	0.58 (0.29)	0.26 (0.08)	0.163 (0.447)	2.04 (0.83)	0.026 (0.038)	0.202 (0.076)	0.107 (0.095)	8.9 (8.1)	80.8 (104.4)	31.6 (33.6)	1.76 (0.90)	385 (318)	442 (441)

Table 2. The percent feedstuffs grown throughout Alberta (A) and near sour gas plants (SGP) that were below the recommended (1R) and below twice the recommended (2R) mineral requirements for pregnant and dry beef cows. (October 1979 to July 1981).

Feedstuff		S		Se		Cu		Mn		Zn		Mo		Fe	
	Recommended Mineral Levels (ppm)	1000		0.1		10		40		50		0.5		50	
		A	SGP	A	SGP	A	SGP	A	SGP	A	SGP	A	SGP	A	SGP
Cereal Roughages	1R	13	0	35	36	93	100	53	71	96	100	18	43	1	0
	2R	82	100	76	64	96		87	100	100		72	57	18	36
Straws	1R	18	0	20	25	100	100	83	100	100	100	55	50	10	0
	2R	91	100	40	50			89				82	75	50	50
Grains	1R	62	75	60	58	93	83	72	64	92	100	47	58	35	22
	2R	100	100	85	92	98	100	100	100	99		77	86	90	67
Hays (Legume, Grass & Mixed)	1R	21	48	30	38	87	94	44	35	98	100	11	11	7	4
	2R	84	93	57	59	99	97	85	94	100		36	55	26	76
Pastures	1R	-	0	-	54	-	70	-	23	-	85	-	0	-	0
	2R	-	61	-	91	-	87	-	77	-	89	-	15	-	4

important for maintaining the total integrity of epithilial tissue. When zinc is deficient in the diet, collagen synthesis is impared (Starcher et al. 1980) or when copper is deficient in the diet, lysyl oxidase activity is reduced which is responsible for the degree of cross-linking in the lysyl residues in collagen and elastin proteins. Reduced tensile strength and elasticity in blood vessels and increased bone fragility have been directly related to copper deficiency (Rucker et al. 1975; Geneger et al. 1976). It has been reported in rats (Duncan and Harley 1978) and suggested in cattle (Geurin 1981) that a vitamin A deficiency syndrome may occur as a result of a zinc deficiency, eventhough adequate levels of vitamin A are supplied in the diet. A vitamin A deficiency is intimately related to reproductive failure in livestock. Therefore, it may be that some of the reproduction problems observed in cattle near SGP and in A are related to a copper-zinc deficiency in the diet.

Assuming feed quality is fair to excellent, animals will consume at least 2% of their body weight in dry matter; it is upon this basis that the minimum concentration of each mineral in a feedstuff is established as a minimum requirement for optimum health, reproduction and production in livestock. However, this minimum required concentration in feedstuff varied among the official organizations who have established the minimum nutrient standards for livestock. As is shown in Table 3, the requirement for any of the minerals is poorly defined. One of the major reasons for these differences is the present lack of understanding regarding mineral availability and mineral interaction in animal metabolism (ARC 1965, NRC 1976, NRC 1978, ARC 1980, Wise 1980).

In order to compare the minerals in Alberta feedstuffs to animal requirements a set of recommend guidelines was established for mineral requirements for ruminants in Alberta. The guidelines were based on presently available standards (Table 3), our experience over the past few years, and the latest research information (Underwood 1981, Smith 1981). These recommend values closely follw the NRC (1978) nutrient requirements of dairy cattle. Furthermore, except for copper in sheep, trace mineral levels twice the recommended minimum requirement (10 ppm) have no adverse effect on ruminant health and

Table 3. Minimum mineral requirements of ruminant animals.*

Mineral	-	NRC DAIRY 1978	NRC BEEF 1976	NRC SHEEP 1975	ARC 1965	ARC 1980	Recommended Levels For Ruminants In Alberta
Calcium	%	0.37-0.60	0.18-0.76	0.21-0.52		0.17-0.67	0.2-0.6
Phosphorus		0.26-0.40	0.18-0.54	0.16-0.37		0.11-0.35	0.2-0.4
Magnesium		0.16-0.20	0.04-0.10	0.04-0.08		0.12-0.21	0.1-0.2
Potassium		0.80	0.60-0.80	0.50			0.8
Sodium		0.10-0.18	0.06	0.04-0.1[illegible]		0.05-0.20	0.1-0.18
Sulfur		0.16-0.20	0.10	0.14-0.26		0.11-0.16	0.1-0.2
Selenium	ppm	0.1	0.05-0.1	0.1		0.05-0.10	0.1
Copper		10	4	5	10	8-20	10
Manganese		40	1-20	20-40	40	10-25	40
Zinc		40	20-30	35-50	50	12-34	50
Molybdenum				0.5			0.5
Iron		50	10	30-50	30	30-40	50

* The range of requirements includes growing animals, mature and lactating cows and sheep. All values given on a dry matter basis.

production but rather may have a positive and beneficial effect, especially during lactation. Copper levels in feedstuffs above 10 ppm may be toxic to sheep if the molybdenum values are below 5 ppm, sulphur levels below 2000 ppm and zinc levels below 50 ppm (Underwood 1981). Excess protein can also reduce the solubility of copper both in the rumen and abmosai digestion of sheep (Ivan and Veira 1981).

When comparing the percentage of feedstuffs near SGP and in A with mineral concentrations below the recommended minimum and below twide the recommended minimum requirement for ruminants, many similarities were recognized. Shown in Table 2, 100% of the cereal roughages, straw and grains had less than twice the recommended minimum levels for S, Cu, Mn, and Zn. Over 93% of the hays had less than twice the recommended minimum levels for S, Cu, Mn, and Zn. Except for grains, over 94% of the stored feedstuffs near SGP had less than the recommended minimum levels of Cu and all the stored feedstuffs had less than the recommended minimum levels of Zn. Over 90% of the samples obtained near SGP and in A for each feed type had Mn levels below the recommended and below twice the recommended requirements.

Over two times the percentage of hay samples obtained near SGP as those obtained in A had less than 1000 ppm S, whereas none of the stored roughage and straw samples had S levels less than 1000 ppm. It has been report that SO_2 emissions alone (Shaw 1981, Murdy and Ragsdale 1980) and SO_2 mixed with other major pollutants (Ormrod et al. 1980, Hofstra and Beckerson 1981) can cause forage tissue damage and increase the S content in forages. There were no cases reported from the farms near the SGP that forage tissue damage occurred due to excessive levels of SO_2 emisions. On the other hand, it has been reported that low SO_2 emisios alone or together with S fertilization may increase forage production significantly (Scott 1979, Walker et al. 1981), decrease Se concentrations (Walker 1971, Westermann and Robbins 1974, Pratley and McFarlane 1974) and in some cases lower soil pH (Shamberger 1981). Although SO_2 emissions may cause tissue damage in forages, the in vitro digestibility of forages damaged by SO_2 emission does not differr with forages not damaged (Milchunas et al. 1981). The feedstuffs obtained near SGP and in A in some cases were deficient to marginal in S contnet for sustaining optimum forage intake (White

1977), including optimum cellulose digestion in cattle and sheep (Kennedy and Siebert 1975). It has been reported that whenever forages contain excessive levels of nitrates S levels exceeding 2500 ppm may be beneficial in preventing nitrate toxicity (Guardiola et al. 1980).

The percentages of stored feedstuffs with selenium levels less than 0.1 and 0.2 ppm were similar for each feed type obtained near SGP and in A. Between 25 and 38% of the stored roughages near SGP and between 20 and 35% of the stored roughages in A had selenium levels less than 0.1 ppm (Table 2). The percent stored roughages with selenium concentrations less than 0.2 ppm varied between 50 and 64% near SGP and 40 and 76% in A. Virtually all the cereal roughage samples near Rocky Mountain House near SGP had less than 0.2 ppm Se (89%) but the percent hay samples with less than 0.2 ppm Se were similar to those obtained in A (67%).

A greater number of grain samples obtained near SGP and in A had less than 0.1 ppm Se than what was observed in the roughages. Again nearly all the grain samples obtained near Rocky Mountain House and near SGP, had less than 0.2 ppm (83%). This observation did not differ from the percentage of barley grain samples with Se levels less than 0.2 ppm obtained over 10 years earlier (80%) (Jacobs 1972, MacDonald and Klemm 1973).

No comparisons between samples obtained near SGP and in A could be made for pastures because very few pasture samples were obtained from farms in A. Compared to the stored roughage samples, the percent pasture samples with less than 0.1 ppm Se was considerably greater, suggesting that selenium deficiency in livestock may be more serious when animals are on pasture than during the late fall and winter seasons when stored feeds are fed.

The high S levels combined with the low Se levels in the pasture samples could aggravate Se availability during digestion by ruminants. Only 61% of the pasture samples had less than 2000 ppm S compared to 93 and 100% of the stored feedstuffs. Not only may S in soils lower the availability of Se to growing forages, but excessive S in forages may lead to an increased incidence of white muscle disease in young ruminants (Paulson et al, 1966, MacDonald and Klemm 1973, Whanger 1979). In other studies it was demonstrated that this may not be true (Hintz and Hogue 1964, Whanger et al. 1968, Brady et al. 1979, Pope et al. 1979). There was no increase in white muscle disease if the Se levels were greater than 0.1 ppm and the S levels did not exceed 2500 ppm, eventhough a S-Se interaction was observed (Whanger et al. 1968).

It must also be emphasized that S (Reddy et al. 1981) and Se (Varo and Koivistoinen 1981, Zieve and Peterson 1981, and personal observation) uptake in forages vary seasonally. Keeping this in mind, together with the possible S-Se interaction especially in years when Se is low and S is high in forages and combined with the individual and/or seasonal variation in salt intake of cattle, when salt is used as a vehicle for Se supplementation (Weber 1981), it is not surprising that Se deficiency problems arise when it is least expected. This would especially be true in areas where Se is quite low and deficient in soils such as those areas west of highway No. 2 and orth of highway No. 16 in Alberta (soil zones 7, 8, 16, and 18).

Except for soil zone 1, more than 70% of the feedstuffs in the other soil zones had mineral concentrations below twice the recommended requirement. Interestingly enough, in soil zone 1 there were no SGP and yet more than 60% of the feedstuffs had S concentrations more than 2000 ppm. Except for soil zones 1, 6, and 16, all feedstuffs in the other soil zones had S concentrations less than 2000 ppm. Most SGP in Alberta are located in soil zones 6 and 8 (Table 4) (MacDonald and Klemm 1973).

In soil zone 6, over 50% of the feed samples had less than the recommended level of S as well as over 45% of the samples had less than 0.1 ppm Se. Similarly over 85% of the samples had less than twice the recommended levels of both S and Se. A similar number of feedstuffs in soil zones 2, 7, 8, 16, and 18 as in soil zone 6 had less than twice the recommended levels of S and Se.

All soil zones, except 18, had greater than 80% of the feedstuffs below the recommended Cu levels for cattle. A similar picture was pbserved for Zn--except for soil zones 2 and 15, Zn was deficient in over 94% of the feedstuffs. Manganese was deficient more severely in soil zones 2 and 16 (80% of the feedstuffs) than in soil zones 1 and 8.

Table 4. Percent Alberta feedstuffs with mineral concentrations below the recommended (1R) and twice the recommended (2R) mineral requirements for pregnant and dry beef cows within the soil areas of Alberta (October 1979 to July 1981).

Soil Zone	Recommended Mineral Levels (ppm)	S 1000	Se 0.1	Cu 10	Mn 40	Zn 50	Mo 0.5	Fe 50
1	1R	20	12	98	29	100	33	2
	2R	40	33	100	75		33	6
2	1R	0	29	80	80	60	--	0
	2R	100	71	100	100	100	--	0
6	1R	53	47	93	63	96	11	20
	2R	87	85	98	94	98	67	52
7	1R	0	33	81	59	94	--	-
	2R	100	80	100	94	100	--	-
8	1R	23	63	80	34	98	50	0
	2R	100	84	99	86	100	87	0
16	1R	43	27	100	80	80	43	33
	2R	86	73		90	100	43	33
18	1R	33	100	67	50	100	20	100
	2R	100		83	83		20	

Molydenum concentrations were not severely deficient in most feedstuffs within soil zones, neither were the Mo levels excessive as purported to be in Manitoba (Smart et al. 1981).

In summary, the mean concentrations of S, Se, Cu, Mn, Zn, and Mo in feedstuffs did not differ between those obtained near SGP and in A. When the concentrations of each mineral within each type of feedstuff was compared to the minimum and twice the minimum recommendations for optimum production in beef cattle, many feedstuffs were deficient. Sulphur concentrations in pastures were 33 to 100% greater and Se concentrations were 42 to 116% lower than those concentrations in stored feedstuffs normally fed in late fall and winter. However, S was not excessive but instead marginal to deficient in many of the stored feedstuffs for optimum livestock production. Most grains and nearly 50% of the hays obtained near SGP S may have been deficient for optimum intake and digestion of cellulose in cattle. Selenium was deficient in 25 to nearly 60% of the various feed types near SGP and was similar to the Se concentrations of the feedstuffs in A. Copper and more particularly Zn appeared to be the most severely deficient in feedstuffs near SGP and in A when compared to the recommended requirements for cattle.

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SESSION V

WORKSHOPS

REPORT ON WORKSHOP I: AIR

Chairpersons: Dr. R.D. Rowe, Department of Mechanical Engineering
University of Calgary
Mr. S. Djurfors, Syncrude Canada Ltd.

1. INTRODUCTION

We had a good workshop with an abundance of stimulating discussion. About 50 people attended this workshop.

A whole day of the Symposium had been devoted to the presentation of papers about the Air System, so we were well primed with information and questions. During his Keynote Address, Jeremy Hales had stressed the interaction of economic and social parameters with any proposed policy to alleviate acid deposition. In particular, he helped to clarify the distinction between a simple roll-back and an engineered "solution" to this problem. This clarification helped us reach a consensus on some quite definitive conclusions and recommendations from this workshop.

To focus the discussion on particular points in a reasonably orderly fashion, we approached pollution in the air systems in terms of each of the conventional components in turn; dry deposition, wet deposition, chemistry, and finally transport and dispersion. Each topic was introduced by an invited speaker, who helped to moderate the subsequent discussion. At least half an hour was devoted to each sub-topic.

Initially, we spent some time convincing ourselves that the above approach was appropriate for this workshop. It is always possible to lose very important constituents to a problem between the cracks of the separate components. There are significant differences between large scale, long term models and smaller scale models and experiments.

How are these models coupled and can they be uncoupled? It was pointed out that our understanding of weather modification is probably more advanced than that of long-range pollution. In studying the problem of weather modification, it is now accepted that component verification is the only way to improve our knowledge of the problem as a whole. With this encouragement, we proceeded to our first topic, that of dry deposition. We worked from receptor to source to see whether a reverse approach would shed any new light on this problem.

2. DRY DEPOSITION

The topic of dry deposition was introduced by Jim Hunt. He started with the good news that for the large scale, long term models, the dry deposition velocity can now be estimated with reasonable accuracy (i.e., within a factor of 2 rather 10). However, for small scale experiments there is still lots of bad news. We are still unable to measure the dry deposition rate of most species accurately, if at all. In those cases where data are available it is not usually possible to make direct comparisons between them because incomplete information has been provided about the multitude of parameters that can influence dry deposition. On the brighter side, a number of promising techniques are under study, and experiments involving many of these techniques at the same site to ensure a valid comparison have been proposed. In the next few years, much effort should be directed towards the development of direct flux measurement methodologies for SO_2, HNO_3, NO_x and particles. Using verified methods, field studies should then be conducted to develop functional relationships between the dry deposition velocity and the resistive elements.

A number of participants emphasized the point that dry deposition is influenced by numerous parameters, including biological parameters. In addition, the complexity of this problem may be compounded by synergistic effects. Much time was spent on this topic, and rightly so, because it appears to be the least well understood component in the entire process.

3. WET DEPOSITION

The topic of wet deposition was introduced by Jeremy Hales. Precipitation scavenging pathways and mechanisms was the subject of his Keynote Address at the beginning of this Symposium. Wet deposition is much better understood than dry deposition, but this is just a relative statement and should not be construed to mean that wet deposition problem has been solved. A continuous long-term record of trends is essential, and, at least, the existing rain-gathering networks should be maintained despite the severity of the current economic recession. Short duration intensive field studies can be very illuminating; the recent investigation of the oxidation and scavenging characteristics of April rain (OSCAR) was cited as a good example. Future studies of this type may only be financially feasible with multi-national support. Further work neds to be done on the analysis of trajectories in storm systems. Losses through the top of storms into the stratosphere may provide a pathway for very long range pollution. Problems related to chemical transformations began to surface during the discussion of this topic; in particular, it was recommended that H_2O_2 and PAN should be measured in future studies.

4. CHEMISTRY

The topic of chemistry was introduced by Jan Bottenheim. Significant progress has been made in the last few years and gas phase air pollution chemistry is now reasonably well understood. However, a major concern has developed recently concerning the oxidation of SO_2 and NO_x in the liquid phase, that is in aerosols and particularly in clouds. Despite a long history, this chemistry is very uncertain to say the least. Kinetics are highly contradictory, and, in fact, even the oxidizing species are not well established.

There is an urgent need for improved monitoring equipment for most species. This refers particularly to nitrogen chemistry, where at present we can monitor NO_x only with specialized equipment, where we have no proven method for measuring NH_3, and where the situation with respect to gaseous and particulate nitrate is a sad saga of uncertainties.

Vertical profiling of the atmospheric flux of pollutants should be given more emphasis in the future. Some very interesting observations were made during the SURE study, in that positive gradients with altitude were observed for sulphate, which are not readily explainable. Another aspect in this regard is the possibility of NO_x in the form of PAN at elevated altitudes.

Some discussion ensued as to whether nitrogen species are important pollutants and some of the proposed effort might therefore be a waste of time. It was agreed that while nitrogen loading may not be important for vegetation, it is definitely an important contribution to the acidification of lakes.

5. TRANSPORT AND DISPERSION

The topics of transport and dispersion were introduced by Boris Weisman and Doug Davidson. Existing parametric models for long-range transport and dispersion work quite well, but they do involve some tuning and require ground level data for verification. There are not enough ground level stations in Western Canada to verify even the current simple parametric models.

Routine monitoring over long periods of time will continue to need considerable attention in the next few years. Such monitoring data are of crucial importance for testing and validating the mathematical models that we employ to assess the impact of pollutant emissions. Too many and too large uncertainties exist in monitoring network data, too many since they would seem unnecessary with some careful planning and execution.

6. CONCLUSIONS AND RECOMMENDATIONS

Although the issue covered in this paragraph was raised earlier in the workshop, it seems more appropriate to report it here. Since it appears that we can already estimate the fate of pollutants within a factor of 2 or so using simple empirical models, isn't the problem solved from the point of view of regulators? This is true in the sense that enough information exists to start implementing some form of simple roll-back policy at this time. However, an engineered approach would provided a much better "solution" in that it should yield a significant gain to society as a whole, over and above that from a roll-back approach (many billions of 1980 dollars per annum). Therefore, the continued investment of substantial research funds into the detailed understanding of this problem is well justified.

It is encouraging to note that the Oil Sands Studies have already made a significant contribution to the international effort. This is all the more encouraging since these activities relate to preventative rather than remedial action by industry and government. How can we in Alberta best continue to make contributions to this problem? We could take advantage of the relatively unpolluted atmosphere in Alberta to study the dry deposition and/or snow chemistry of individual pollutants. In particular, we should capitalize on our existing expertise in the subject area of convective storms to undertake studies of pollutant chemistry within these storms. Finally and internationally, the most urgent need seems to be to find ways of encouraging chemists to become involved both in the development of new measurement techniques and in pollutant chemistry particularly in the liquid phase.

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REPORT ON WORKSHOP II: AQUATIC

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1. INTRODUCTION

The overall objective of the workshop was determined to be "to identify a relevant research program for western Canada on the potential effects of acidic deposition on aquatic ecosystems.

In formulating an approach to the identification and development of this research program, it was recognized that its success was contingent upon two key factors:

1. The program must maintain a western Canada focus
2. Management without proper scientific basis is meaningless

The following summarized results from the workshop identify a scheme for the recognition of the research needs, and subsequent development of a relevant research program, for western Canada.

2. DEVELOP REGIONAL MAPS OF THE POTENTIAL FOR WATERBODY ACIDIFICATION

An essential prerequisite to assessing the possible effects of acidic deposition on aquatic ecosystems is the preparation of regional maps indicating degrees of acidification potential. The parameters used to determine acidification potential are to be based on physical (geographical/geological), chemical, and biological variables.

The proposed procedure for the development of these maps is:

1. Qualitative Overview. A qualitative overview will identify the physical, chemical, and biological parameters that can be used for the evaluation of acidification potential, and determine indices for mapping.

   The Coordinating Committee on Surface Waters of the Technical Committee on Western Canada Long Range Transport of Air Pollutants has identified available information, desirable elements, and information gaps relevant to sensitivity mapping. This committee has prepared recommendations for sensitivity mapping that identify many of the chemical components needed for this overview (Appendix 7.1).

The soil/sediment/water interface was recognized as an important consideration in the identification of acidification potential indices. Of particular concern are the effects of aluminum, heavy metals (Fe, Hg, Mn, Cu, Mg), organics (humic and fulvic acids), and anthropogenic metals (Pb, Cd, Ni, V, radionucleides).

2. Measures. The next step in the development of regional maps is the measurement of the parameters identified as being related to acidification potential. A proposed research pathway for western Canada is:
    a) conduct a wide regional survey of waterbodies;
    b) conduct a calibrated watershed study on a select area;
    c) use the data for the development of further techniques and methodologies.
3. Models. The development of models enables the procedure to progress from strictly analytical measurements to predictive capabilities. A calibrated watershed model will incorporate input, output, and dry and wet deposition resulting from acid forming emissions.
4. Classify Watersheds. Potential acidification measurements and model predictions can be used to develop a watershed classification scheme for mapping purposes.
5. Validate. Continual validation of the models and classification scheme will allow input of knowledge back into the qualitative overview, setting up a feedback loop that will ensure constant improvement and precision of the mapping technique.

The development of this mapping procedure is vital to the understanding of the watesheds before acidic deposition occurs, and is necessary to the formulation of a research program for western Canada.

3. SOURCES OF EMISSIONS

With the mapping procedure established, information on the point sources and scenarios of deposition can be introduced into the models.

4. TRANSPORT MECHANISMS

Meteorological information and network models can also be fedback into the aquatic models.

5. MANAGEMENT FRAMEWORK

The management framework must be interprovincial, and perhaps even national, in nature. It is also necessary to ensure a mechanism for interface with the industries involved. The Alberta Petroleum/Government Environmental Committee (APIGEC), aquatic Steering Committee on Acid Gases in the Environment (SCAGE) has made recommendations to the government and industry, and are awaiting a response.

Recommendations for further study complied with those put forth by the western Canada LRTAP Coordinating Committee on Surface Waters are described in Appendix 7.2.

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7. APPENDICES

7.1 RECOMMENDATIONS FOR SENSITIVITY MAPPING (Sawchyn 1982)

1. On the basis of data available, preliminary sensitivity mapping should proceed as follows:
    1. Mapping of alkalinity and calcium, or Calcite Index to outline the buffering capacity of surface waters and thereby the sensitivity to acidification to complement similar mapping programs undertaken elsewhere in Canada;
    2. Sensitivity rating advocated by Altschuller and McBean (1979) and NRCC (1981) should be used to provide continuity with studies already completed.
2. Mapping using pH should be undertaken to determine the state of acidification to date. In recognition of the potentially severe limitations of these data, only the five most recent years of data should be used.
3. Numerous data are available for rivers and streams in addition to the lake data provided. In areas where appropriate coverage is not derived from lake data, discretionary use of stream data may be appropriate provided that they represent geochemically homogenous watersheds.
4. The majority of data points are represented by only one measurement. Those with more than one measurement are taken over a variety of depths, lake locations, seasons or periods in one season resulting in a poor statistical data base. Recognizing these limitations, we recommend that the median be taken of the available pH, alkalinity and calcium measurements for any point or group of sampling stations in a lake.
5. Sensitivity mapping should be undertaken on a map scale of 1:2 000 000. This scale allows reasonably accurate identification of sampling sites. It would provide a degree of accuracy consistent with the quality of the available data base. With some slight reduction this scale could be accommodated in report format either by province or the entire region.

7.2 RECOMMENDATIONS FOR FURTHER STUDY (after Sawchyn 1982)

1. Each jurisdiction should undertake an extensive lake sampling program to provide new data for those areas where no data exist and to update the existing information base to the extent that reliance on data older than five years should not be required.
2. The information update should focus on more sensitive areas in the northern environment.
3. The data base should include representative and standardized measurements of pH, alkalinity, calcium, magnesium, specific conductivity, and an appropriate form of aluminum.
4. The data base should include measurements of lake surface area and maximum depth. Where new measurements are required the lakes should be selected so as to provide a range of sizes representative of each geographic area. If the scope of the survey must be limited, smaller headwater lakes should be selected.
5. Each jurisdiction should maintain a comprehensive data bank to handle existing and new surface water quality data. Data acquisition, manipulation, and interpretation could be facilitated if the data bases could be consolidated on one computer system.
6. The applicability to the program of the mapping capability of the NAQUADAT computer program available through the Water Quality Branch of Inland Waters should be investigated.
7. The data base should include measurements from wetland areas.

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REPORT ON WORKSHOP III: TERRESTRIAL

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1. SUMMARY

The Terrestrial Workshop was attended by approximately 35 persons from government, industry, academia, and the public.

The group was divided into four sub-groups, each with a chairman, and provided with a set of four questions. The sub-groups were asked to address each of these questions during a specified time. The four questions were:

1. Given the existing resource development scenario for Alberta, what do you think the impacts of acid forming emissions on terrestrial ecosystems are likely to be? Please list and prioritize. (15 mins.)
2. Do you believe that any of these impacts are occurring now? What is the evidence? (15 mins.)
3. With reference to the list developed under item 1, how could the suspected impact be quantitatively verified, i.e., what parameters should be measured, where should they be measured, how should they be measured, etc. (30 mins.)
4. List and prioritize research needs in this area. (30 mins.)

The final portion of the workshop was allotted to comparison of sub-group priorities identified under question four and discussion of these priorities.

The results of the exercise were quite encouraging. The four sub-groups identified very similar research needs in isolation. Emphasis and detail varied somewhat, depending upon the expertise within each sub-group. As well, the research needs identified were similar to those recommended by past committees that have addressed the problem (e.g. Steering Committee on Acid Gases in the Environment (SCAGE); ad hoc Committee on sulphur and soils).

Present research in the province is addressing many of the identified problems. It was agreed by the group that more research is needed.

2. RECOMMENDATIONS

The group compiled a list of seven major research needs. It became obvious that there was some overlap among the identified research areas. There were also differences in time scale in that some results could be achieved in a short time period while other problem areas would require long-term research studies. Individual research needs would have to be addressed in sequence in some instances. While a particular problem area might be considered extremely urgent, some preliminary work might have to be carried out in another field (e.g. methodology; technology) before that problem area could be properly addressed. Therefore, it was difficult to prioritize research needs and the final concensus was that this should not be done.

The seven major research areas identified were as follows:

1. Deposition
   - Distribution
   - Species
   - Quantify and Rate
   - Mode of Entry
2. Methodology
   - Sampling
   - Analysis
   - Parameters/Variables
   - Technique
   - Standardization
3. Characterization and Quantification of Dose Response
   - Time
   - Space
   - Receptors
     - Soils
     - Vegetation
   - Assimilitive Capacity
   - Threshold Levels

Sensitivity of Species
Sensitivity of Receiving Areas

4. Pathways and Processes
   Buffering Capacity
   Acidification
   Nutrient Cycles
   Toxicity
   Organic Decomposition
   Productivity
5. Mitigation and Amelioration
6. Prediction of Effects
   Biological Monitoring
   Physical (mechanical) Monitoring
   Modelling
7. Associated Effects
   Identification and Quantification of Natural, Cultural and Industrial Processes.

In summary, physiological and ecological effects on forestry, agriculture, and wildlife.

A good time was had by all!

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REPORT ON WORKSHOP IV: HEALTH

Chairpersons: Dr. P. Barnes, Shell Canada Resources Ltd.
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1. SUMMARY

The objectives of the workshop were to review the published and completed research and the present ongoing research on the effects of acid emissions on human and animal health, together with recommendations for further research needed in Alberta. Discussion was invited in the areas of the direct effects and indirect effects of acid emissions on the health of man and animals.

Considerable discussion arose concerning the direct effects of acid emissions upon health. The published research has been included in this report. The projects underway in Alberta are few.

There was an expressed need for a study of the causations of mortality and morbidity of humans within various communities of Alberta. However, it was argued, the number of variables such as occupation, personal habits, nutrition, marital status, etc., would be difficult to remove in order to determine whether acid emissions or any other pollutant would affect the health of populations. It was further argued that in comparing mortality and morbidity status among community centers the size, density, location, and dynamic movement of populations were other variables difficult to remove to determine if acid emissions from a given source were affecting the health of a population. Nevertheless, it was still felt by most of the participants (about 20) that an epidemiological pilot study should be started soon to get some idea of the incidence of specific diseases within selected communities in Alberta.

It was also observed by some participants that in those situations where human health problems appeared to exist together with a suggested association to acid emissions no adverse health problems appeared to coexist in household pets or farm animals of the complanant families.

Research of the literature was needed to see if research in other areas of the world (especially Europe and New Zealand) have reported a direct association with acid emissions to human and animal health. This information would aid research scientists in Alberta to build models which could help to focus on those areas where further research is needed most.

It was also suggested that more stack and flare emision samples need to be collected from various emission sources and analyzed for content including mineral levels to assure Albertans of their confidence levels.

It was further suggested that better biological predictors are needed to help decision makers evaluate the impact of new industrial and commercial developments. The information derived from animals and man exposed to short term and high concentrations of acid emissions are not good predictors of long-term chronic exposures. It was also felt that long-term research efforts of acid emissions on human and animal health would ellucidate the real and perceived effects that are not now understood. After many years of research, for example, on the age-old problem of alcohol consumption, it is now becoming evident from a scientific basis that the alcohol effect on health and behaviour in man is not only real (has physiological effects) but also perceived (The Think-Drink Effect; G.A. Marlatt, and D.J. Rohsenow; Psychol Today, Dec. 1981, p. 60).

Discussion regarding the indirect effect of acid emissions upon the health of man and animals was less enthusiastic. Considerable research on the effects of sulphur and its various compounds associated with various feedstuffs suggests that sulphur is not only an essential element in nutrition, but it interacts in digestion with other elements such as copper, molybdenum and selenium, affecting their subsequent availability. In the feed sampled and analyzed near sour gas plants thus far, it appears that sulphur in feeds is not toxic to animals but on the contrary, marginal to deficient, and in many cases needs supplementation in the diets of animals to optimize digestion of fibrous feeds. As far as the effects of sulphur on the availability of other elements such as copper and selenium, it has been thought to be neglible, based on research done so far. It is very apparent that feeds in many areas of Alberta are deficient in selenium, copper and zinc, and micro-mineral supplementation is necessary for optimizing livestock production. Several cases of copper and selenium deficiency have been diagnosed near sour gas plants and in other areas of the province not associated with sour gas plants. Selenium deficiency problems have been recognized in several areas of the province for over 15 years.

As a result of problems arising from several farms near Rocky Mountain House, but not unique among farms in other areas of the province, a pilot study has been undertaken by a group of scientists from various agencies and departments including the Alberta Environmental Center and Alberta Agriculture. This pilot study has investigated four farms and its results are reported in the proceedings of this symposium. The remainder will be available as soon as they are analyzed and studied. Upon the completion of this report an evaluation will be made and further research efforts will be proposed.

2. RECOMMENDATIONS

In summary, the participants of the workshop agreed on the following recommendation:

1. First, determine whether a problem exists. Is the problem being expressed, real or perceived?

In the determination of these problems the following strategies were suggested, not necessarily in the order listed.

1. Case studies are necessary to determine if a clustering of similar problems and pollution complaints are occurring or have occurred.
2. Epidemiological comparisons between various communities in Alberta are needed regardless of the difficulty of removing the high variation within and between communities.
3. Baseline information, which may include epidemiological information, air quality measurements, local flora, and fauna studies and soil analyses, should be available before major developments (refineries, industry, cites,

etc.) become operational. (No effort on behalf of the workshop was expanded on what and how much baseline information is required.)

4. Laboratory investigations regarding the effects of individual and interacting pollutant gases, liquids and particles on animals and man are needed, especially within long-term time limits.

Arising from the discussions it became apparent that the following recommendations need to be implemented immediately.

1. A group of individual scientists from a variety of disciplines as well as individuals from the general population need to form a working group who would be solely responsible for developing, coordinating, directing, implementing and reporting the results of the research based on the above recommendations.
   This group of people (Coordinating Committee) is already in the process of being formed and needs medical and public input (The Environmental Centre at Vegreville, Alberta).
2. A series of communication routes needs continued development between the Coordinating Committee and the private consultants and scientists and between the Coordinating Committee and the general public.
   Information transfer from the public sector to the Coordinating needs to be developed to a greater degree especially in listening and recording of their problems.
   Information transfer from the scientists to the general public also needs more emphasis and effort.
3. Information transfer from private companies to the general public needs to be emphasized much more than it is presently, and especially within the communities where private developments exist. It is too often assumed by the private sector that the general population within the communities know what is going on within the industrial complex. There needs to be a continued effort on the part of industry to acquaint

everyone within community exactly what the plant is manufacturing and the processes and chemicals involved and as to the various emissions and their control. When no communication occurs between private industry and the general public, a mistrust soon develops and fear of the unknown becomes a powerful motivating force for the removal of private industry from the community.

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